ABSTRACT

A Fuoss-Mead membrane osmometer was modified for routine laboratory use so that it offered a number of advantages over the original design. The main improvements included the filling device which permitted the injection of samples by syringe, and two precision-bore capillaries of small internal diameter to measure very small liquid volume changes. Micro-needle valves were used as volume regulators to permit the independent adjustment of the liquid level in either capillary.

Pure solvent flow through various membranes was studied using tetrahydrofuran and cyclohexanone as solvents. Cellulose derivative membranes of the Schleicher and Schuell 08 type were found quite suitable for use with tetrahydrofuran whereas with cyclohexanone flow was somewhat restricted.

Osmotic pressures of three grades of commercial polyvinyl chloride (PVC) dissolved in tetrahydrofuran were measured at 25°C. These pressures ranged from 0.14 to 3.57 cm. of equivalent liquid head of solvent. A modified Bruss and Stross dynamic method was devised for measuring osmotic pressure and it compared favourably in speed and consistency with conventional methods. It consisted of taking sets of readings of both capillary levels by means of a cathetometer and observing the rate of change of these levels during fixed time intervals for a number of different hydraulic heads. A least mean squares fit was then used to determine the equilibrium osmotic pressure head from the hydraulic head and corresponding rate of change of hydraulic head data.

One of the commercial samples of PVC was separated into its constituent fractions by fractional precipitation. Each fraction was then analysed by osmometry, and viscometry, to obtain the number-average, and weight-average molecular weights, respectively. Molecular weight distribution curves for the fractions were constructed and the distributions were found to agree well with the experimentally determined number-average and weight-average molecular weights for the original composite sample.

The measurement of osmotic pressure and viscosity provided a simple but effective means of characterizing samples of PVC. Other methods of characterizing polymers are generally more time consuming and require expensive equipment which must be calibrated. It is hoped that the equipment and techniques devised in this research may be further utilized for routine laboratory testing of PVC samples.

ACKNOWLEDGEMENT

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INTRODUCTION

High polymers such as polyvinyl chloride (PVC) generally contain molecules having a wide range of chain lengths. Because each of the molecular species in a sample contributes to the overall properties of that sample, a knowledge of the molecular weight distribution is essential for predicting polymer properties. Frequently, high product quality and consistency of properties require that all molecules be similar in chain length or have a narrow molecular weight distribution. It is possible to measure the breadth of a molecular weight distribution (or its dispersity) by a combination of osmotic pressure and viscosity measurements which therefore can be useful for quality control purposes in the production of polymers.

Different statistical averages can be used to describe a particular molecular weight distribution. The average which represents the most probable molecular weight of a sample, is called the number-average molecular weight and is defined as:

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

This definition shows that each molecule exerts the same influence on the molecular weight regardless of its mass. Properties dependent upon the number of molecules in solution are known as colligative properties and, therefore, bear a direct relationship to the molar concentration. For a dilute polymer solution osmotic pressure is relatively large when compared with other colligative properties. This makes it useful for determining the number-average molecular weight. Changes in boiling or freezing points or changes in vapour pressure resulting from the solution of a polymer in a solvent are extremely small and quite difficult to measure.

The weight-average molecular weight emphasizes the weight of individual molecules when represented on a weight-molecular weight distribution. It is defined as:

$$\overline{M}_w = \frac{\sum w_i M_i}{\sum w_i} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

It is generally determined by measuring the degree of light scattering in polymer solutions. In such measurements, the scattered light is dependent upon the total area of molecules which intercept a beam of light. Instruments for making such measurements are quite costly and require precise calibration.

The viscosity-average molecular weight is defined as:

$$\overline{M}_v = \left(\frac{\sum n_i M_i^{m+1}}{\sum n_i M_i} \right)^{1/m} \quad \ldots\ldots\ldots\ldots (3)$$

where m is a constant depending on the particular polymer and solvent used. It is obtained by measuring the viscosities of dilute polymer solutions.

A fourth type of statistical average for a molecular weight distribution is the Z-average molecular weight which is defined as:

$$\overline{M}_Z = \frac{\sum n_i M_i^3}{\sum n_i M_i^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

It is determined by an ultracentrifuge which measures the rate of sedimentation of polymer out of solution when the solution is subjected to high centrifugal force. The apparatus for such measurements is complex, and the measurements are time consuming.

The molar-molecular weight distribution curve for a polydisperse polymer is generally asymmetrical about the peak as indicated in Figure 1.(1) The relative positions for the four types of averages are also shown qualitatively in Figure 1. For a monodisperse polymer sample all four of the averages are identical.

Because the number-average and weight-average molecular weights differ for a polydisperse sample the ratio $\overline{M}_w/\overline{M}_n$ affords a means of measuring the degree of polydispersity or breadth of the molecular weight distribution.

An osmometer is a useful instrument in the characterization of a polymer because it can be utilized to determine the number-average molecular weight. Of the several types, all are simple in design and do not require calibration. In these instruments equilibrium is approached by allowing solvent to pass through a semi-permeable membrane into a polymer solution. The osmotic pressure is measured as the hydraulic head of solution which is just required to prevent osmosis from occurring. The number-average molecular weight is calculated from the van't Hoff relationship discussed in the theory.

Gel permeation chromatography, a more recent development, provides a molecular scan of the entire molecular weight range. The instrument requires precise and time consuming calibrations with mono-

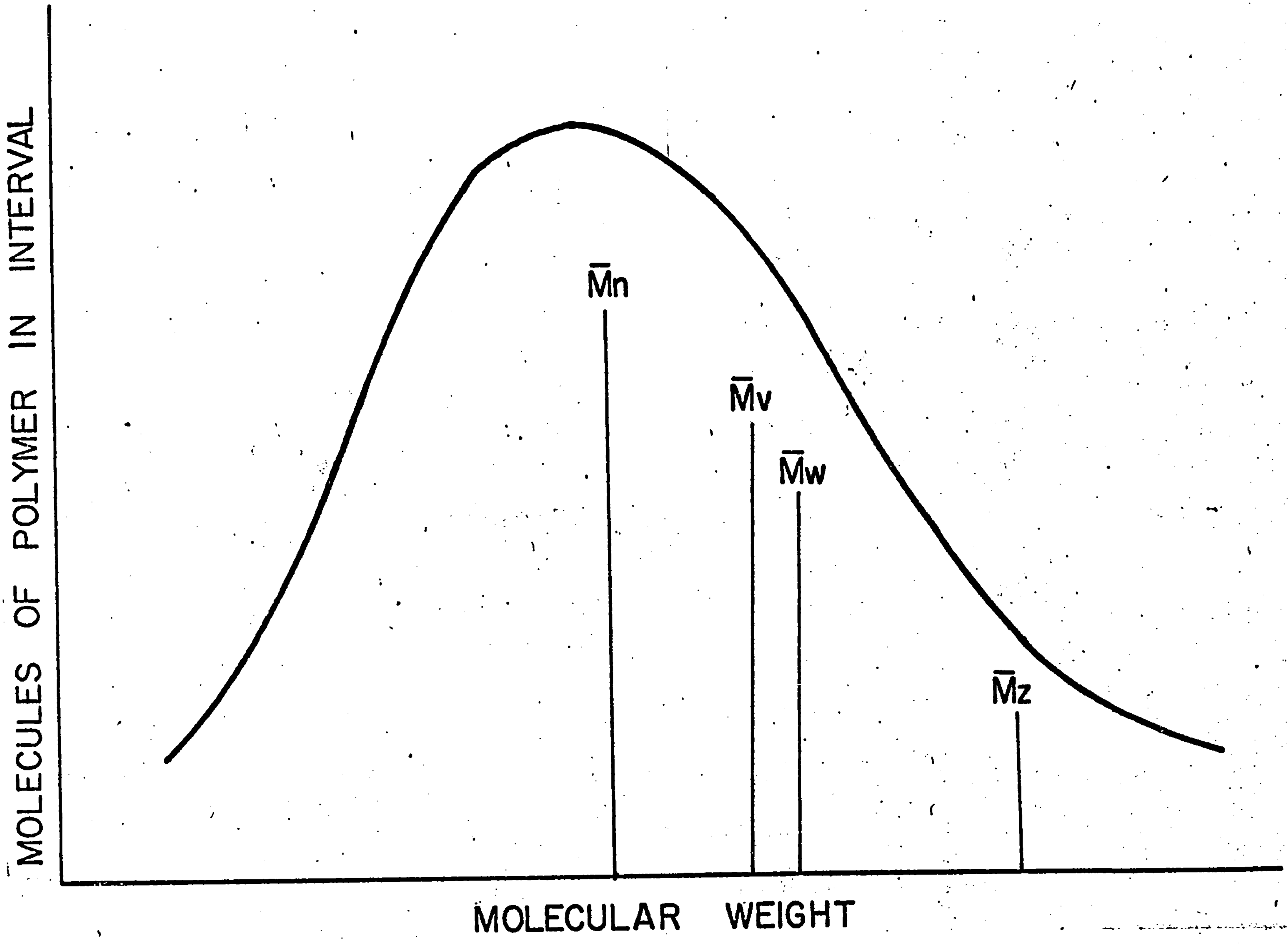

Figure 1 - Distribution of various molecular weight averages about the mean.

disperse fractions to cover the entire molecular weight range. Often such monodisperse fractions are not available.

The scope of this work included the design and construction of an improved osmometer to make possible the routine analysis of PVC. Most commercially available osmometers are difficult to use for routine measurements because the solution and solvent require a considerable length of time to reach equilibrium. They are also difficult to assemble and operate. An improved osmometer was constructed to speed up the approach to equilibrium by adjusting the meniscus levels. It was also simple to assemble and fill and this made it valuable as a laboratory instrument.

Also attempted in this work was the fractional precipitation of a commercial polymer sample to determine its molecular weight distribution by actually separating the sample into constituent fractions. The positions of the number-average and weight-average molecular weights of the original sample were verified. The choice of the particular polymer grade used for this study was based on the presumption that higher molecular weight polymers generally have a wider distribution of molecular weights.

THEORY AND LITERATURE SURVEY

A. OSMOMETERS AND OSMOTIC PRESSURE

Osmometers permit the measurement of osmotic pressure in terms of hydraulic head required to prevent flow of solvent through a semi-permeable membrane into a polymer solution. Such a flow would otherwise tend to occur to equalize the chemical potentials with respect to solvent in both solution and solvent until both sides were of equal concentration. The driving force causing such flow is the difference in solvent concentration between the solution and solvent or indirectly the molar concentration of polymer in the solution.

Osmometers are of many types. The simplest was proposed by Schultz (2) and merely consisted of an inverted thistle tube, the bottom of which was covered with a semi-permeable membrane (impermeable to solute). The tube was filled with solution and immersed in excess solvent. Equilibrium was established by solvent flow through the membrane into the solution and was observed as a hydraulic head in the neck of the tube. Such an instrument is known as a static osmometer because an equilibrium measurement is made corresponding to a condition of no net flow through the membrane. Its main disadvantage is the long time required to reach equilibrium. Improvements to the basic design were made by Wagner (3) which included the use of a small capillary tube to observe the osmotic pressure and a smaller solution chamber. These changes reduced the equilibration time because less solvent was required to flow through the membrane for a given change in hydraulic head.

Another static osmometer was later developed by Berkeley and Hartley (4) to measure osmotic pressure indirectly. Two chambers for solution and solvent were separated by a rigidly supported membrane. A pressure was induced on the solution side until no further flow of solvent was detected. This measurement of osmotic pressure eliminated much of the time required for osmosis to actually occur.

The dynamic method for osmotic pressure measurement was first reported by Fuoss and Mead (5). In this method the hydraulic heads in the solution and solvent chambers are pre-adjusted and their change with time is observed. Their osmometer consisted of two metal plates with concentric grooves on the face of each. A membrane was rigidly supported between these faces when the plates were clamped together. Solution and solvent, respectively, were placed in the grooves of each face in contact with the membrane. A capillary tube was provided for use on one chamber to measure hydraulic head the level of which could be adjusted by inserting a rod into the capillary to displace the liquid. The other chamber was provided with a simple glass filling tube,in which the level was adjusted by addition or removal of liquid. The advantages of this instrument were its small internal volume and all-metal construction which made it durable.

Zimm and Myerson (6) reported the design of another type of osmometer which attained equilibrium quite quickly. The Zimm-Myerson osmometer utilized two membranes in conjunction with a glass solution cell. This cell was made from heavy-walled glass tubing to which capillary tubes were connected for filling and measuring purposes. Bubbles were easily detected and removed in such a cell. A membrane was clamped to each side of the cell by means of perforated metal plates. The instrument was filled with solution and immersed in a solvent bath permitting solvent to contact the membrane through the holes. Means were also provided for the adjustment of the capillary meniscus level. The disadvantage of this type of instrument would appear to be that it was fragile and membranes were not well supported so that movement of the membrane resulted. The large solution volume made the instrument sensitive to temperature fluctuations which resulted in thermometric effects in the capillary. In addition, the procedures for filling and assembling the instrument were extremely difficult.

A more refined osmometer was developed by Pinner and Stabin (7) which utilized a longer filling tube so that solution could be introduced into the instrument while in the vertical position and without removing it from the solvent.

The Pinner and Stabin osmometer was further modified by Stabin and Immergut (8) to hold larger membranes. In addition, each membrane was rigidly supported on both sides by pairs of perforated plates. They provided a larger membrane area and facilitated the approach to equilibrium. The cell was filled by means of a hypodermic syringe fitted with a long needle. A disadvantage of the instrument was its relatively large cell volume.

Several block type osmometers have been developed in more recent times (9). These were generally modifications of instruments already described. Of these, the Bruss and Stross instrument (10) was of particular interest and some features of this instrument were used in our design. Basically, it offered the same advantages as the Stabin-Immergut version. However, the cell body was constructed of stainless steel and the volume was much smaller. As a result, thermometric effects were nearly eliminated. The rugged construction made it suitable for constant laboratory use.

In designing an osmometer, consideration needed to be given to a number of factors some of which have already been mentioned (11).

a) Accuracy

Osmotic pressures of high polymer solutions are quite small and meniscus levels must therefore be read accurately using a cathetometer. Moreover, the capillaries themselves need to be of uniform bore to prevent differences in levels in the capillaries resulting from different capillary forces.

b) Rapid operation

Rapid results are essential if an osmometer is to serve a useful purpose as an instrument. Otherwise, valuable research time is consumed. The rate of approach to equilibrium depends on the ratio of the effective membrane area to the capillary cross-sectional area. For a given osmotic pressure the volume of liquid which must pass through the membrane is proportional to the cross-sectional area of the capillary, and the rate of transfer is proportional to the exposed membrane area.

c) Provision for pre-adjustment of levels

Osmosis is a slow process and the time required to reach equilibrium can be reduced if the levels can be first set close to the expected equilibrium positions. A provision for pre-adjustment of capillary levels is also useful for dynamic methods for measuring osmotic pressure.

d) Elimination of thermometric effects

The cell volume must be small for a given capillary cross-sectional area. Otherwise, changes in the relative volume of the cell contents due to temperature fluctuations result in significant changes in meniscus levels. These thermometric effects can be reduced if the coefficients of expansion of the osmometer and its liquid contents are of the same magnitude. Precise temperature control is also required to prevent such volume changes. If temperature fluctuations do occur, they can be dampened by using a cell with a large heat capacity.

e) Elimination of air bubbles

Air bubbles should be readily detected and removed; otherwise the position of the meniscus levels no longer represents equivalent hydraulic heads causing errors.

f) Ease of filling

For routine measurements an osmometer should be easily filled without having to be dismantled.

The osmotic pressure of a polymer solution is a colligative property dependent upon the number of molecules in solution. It is related to the molecular weight by the van't Hoff equation (12, 13):

$$\pi = \frac{cRT}{M} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

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

$$\left(\frac{\pi}{c}\right)_{c \to 0} = \frac{RT}{M} \quad \ldots\ldots\ldots\ldots\ldots (6)$$

For dilute polymer solutions (less than 1 weight %) equation (6) is linear in c and includes an extra term as follows:

$$\frac{\pi}{c} = \frac{RT}{M} + Bc \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

At higher concentrations this equation is not linear. In the range of low concentrations a plot of π/c versus c has a slope B which depends upon the solute-solvent interaction (13).

Osmotic pressure is observed as a hydraulic head, H, across the membrane from which it is possible to calculate on osmotic pressure for use in equation (7). The usefulness of equation (7) is that osmotic pressures obtained in several experiments at different concentrations can be extrapolated to zero concentration to determine the molecular weight. For a polydisperse polymer sample M in the van't Hoff equation is actually the number-average molecular weight, $\overline{M}_n$.

B. MEMBRANES

Reliable osmotic pressure measurements are limited by the availability of suitable membranes. A membrane must be impermeable to solute yet permit flow of solvent so that equilibrium may be approached. The membrane must retain all the solute, or at worst, allow solute to diffuse slowly enough so that the rate of solvent transfer can be measured; otherwise the membrane is useless. The static or equilibrium type of osmotic pressure measurements imposes the most severe requirements because a long time elapses between filling the osmometer and reading the capillary meniscus levels. During this time slight solute permeation may occur and decrease the solution concentration. Also, a slight osmotic pressure will develop on the solvent side of the membrane. In fact, according to Staverman (13) even molecules, which are capable of permeating the membrane but do not actually do so, do not contribute fully to the osmotic pressure measurement.

Membranes used for osmotic pressure measurements have a porous gel structure. Flow of solvent through the membrane occurs through the membrane pores and may be interpreted in terms of the familiar Hagen-Poiseuille equation (14):

$$Q = \frac{\pi (\Delta P) R_a^4}{8 \eta L} \quad \dots\dots\dots\dots\dots\dots\dots \quad (8)$$

If it is assumed that a membrane of thickness L is made up of n straight pores each having a radius of R_a cm., the flow through each pore is expressed by equation (8). The effective flow area is $n \pi R_a^2$ and may be expressed in terms of the total membrane area A and porosity ε:

$$n \pi R_a^2 = \varepsilon A \quad \dots\dots\dots\dots\dots\dots\dots \quad (9)$$

Porosity normally expresses the ratio of pore volume to total volume. If the pore length and membrane thickness are equal, the porosity expresses the ratio of pore area to membrane area. When the flow of solvent through a membrane is measured in an osmometer it may be expressed as the rate of decrease in hydraulic head, h, times the capillary cross-sectional area, a:

$$-\frac{dh}{dt} a = \frac{\varepsilon h d_1 g A R_a^2}{8 \eta L} \quad \dots\dots\dots\dots\dots \quad (10)$$

Combining all constant terms a permeation constant k_p can then be defined (15):

$$-\frac{dh}{dt} = k_p h \quad \dots\dots\dots\dots\dots\dots\dots \quad (11)$$

This permeation constant is useful for characterizing membranes provided the same osmometer is used for all measurements.

Membranes are usually supplied in an aqueous ethanol solution, and it is necessary to condition them gradually to the final solvent to be used. Otherwise the porous structure of the membrane may be damaged (16). For a membrane to be effective in permitting solvent transfer the solvent must swell the membrane and open the pores (17). The gradual conditioning of the membrane to the final solvent is carried out in a series of solutions in which the solvent concentration is increased. In this way, the membrane structure is altered gradually. Alvang and Samuelson (18) have found that some solvents do not swell certain membranes. A membrane is chosen for a particular polymer-solvent system only if the solvent swells the membrane.

During osmosis the flow of solvent through a membrane occurs by a process known as passive transport (19). The sieve-like action of the membrane pores allows solute particles to enter the membrane but not to pass through. A concentration gradient gradually develops across the membrane and is maintained by the random motion of solute molecules. As a solvent molecule enters the membrane from the solvent side it associates with a solute molecule and causes further membrane swelling. This causes solvent to flow towards the solution side until equilibrium is established or until a hydraulic head is built up on the solution side to prevent further flow.

Certain membranes exhibit an osmotic pressure head even with pure solvent on both sides. This is known as an asymmetry pressure and is caused by irregular membrane structure and an uneven distribution of solvent molecules. Corrections must be made to osmotic pressures to account for membrane asymmetry (20).

C. METHODS FOR MEASURING OSMOTIC PRESSURE

The static or equilibrium measurement of osmotic pressure is the simplest method available for determining osmotic pressure. The main disadvantage of this method is that it is time consuming. The rate of approach to equilibrium is proportional to the concentration difference across the membrane; hence, when an osmotic pressure head develops, it opposes flow through the membrane and the rate decreases. As a result the length of time for attaining an equilibrium osmotic pressure is considerable.

To make routine measurements possible a rapid dynamic method was proposed by Fuoss and Mead (5). It involved pre-setting the capillary meniscus levels at some positions other than the expected equilibrium positions. In the method osmosis was permitted to occur and readings taken at various times were subsequently plotted. From the dynamic response curve an approximate value of H was estimated. The levels were than set a similar distance from the expected H but in the opposite direction. Again equilibrium was approached and a dynamic response curve plotted. The half-sum of both response curves was plotted and the asymptote extrapolated to zero time to obtain an estimated osmotic pressure. In certain cases it was found necessary to repeat one of the runs to obtain a better asymptote (see Figure 2).

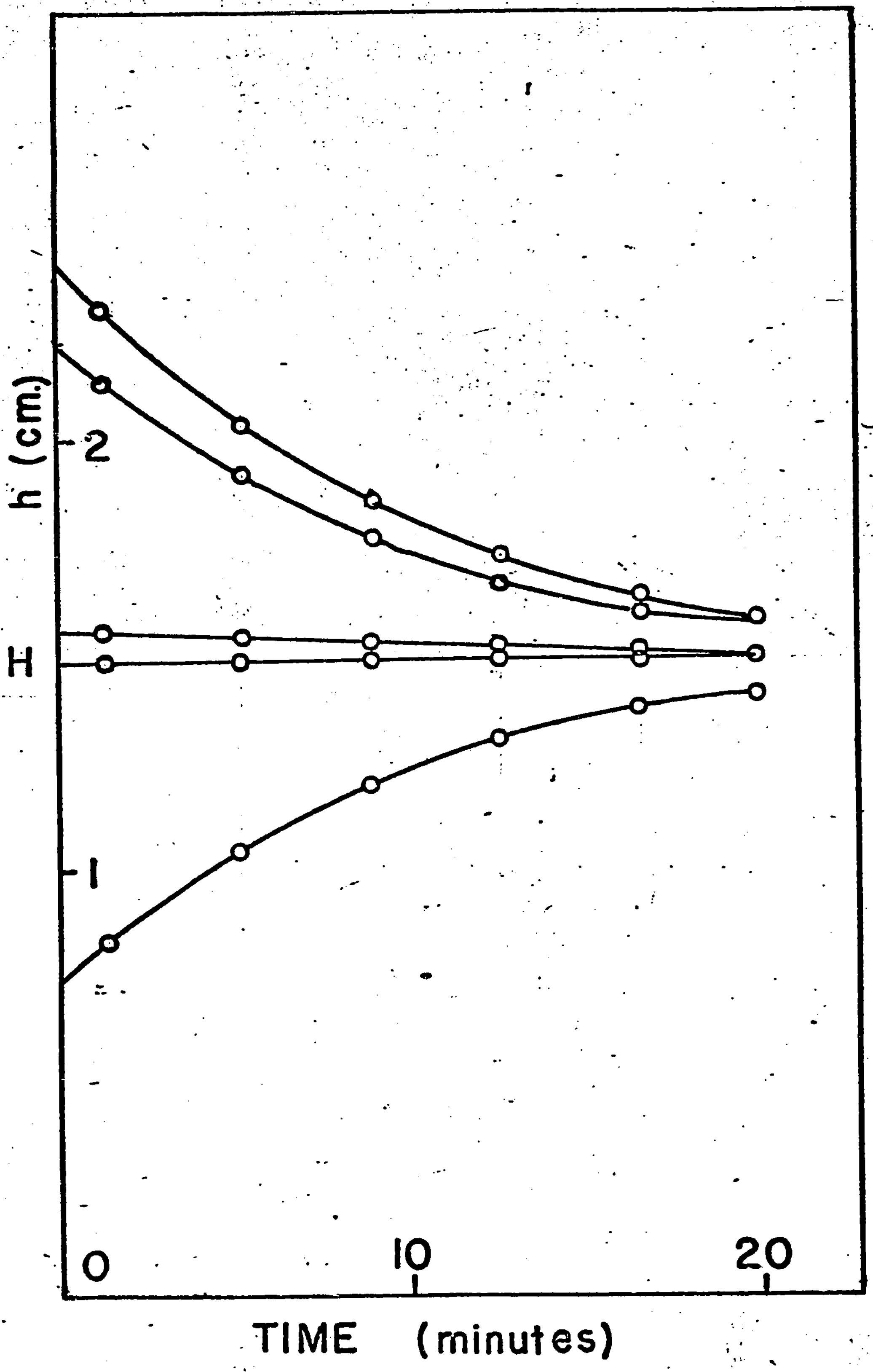

Figure 2 - Illustration of the Fuoss-Mead Method.

The method of Philipp (21) was based on the assumption of an exponential decay in the hydrostatic head, h. If readings of h were taken at three equally spaced time intervals, then the osmotic pressure head could be obtained from:

$$H = \frac{h_1 h_3 - h_2^2}{h_1 + h_3 - 2h_2} \quad \ldots\ldots\ldots\ldots\ldots (12)$$

This method gives a good approximation for use in the Fuoss-Mead method. An advantage was that only three readings were required. However, the method was not reliable when permeating solute was present.

The Bruss and Stross method (22) consisted of timing the movement of the meniscus levels (flow through the membrane) between two given points to determine the rate of change of h as a function of h. An alternate approach was to obtain the data from a dynamic response curve such as recorded for the Fuoss-Mead method. Since the flow was stopped at equilibrium when h was equal to H, the driving force was actually h-H. Equation (11) could be then written in the form:

$$-\frac{dh}{dt} = k_p\,(h-H) \quad \ldots\ldots\ldots\ldots\ldots (13)$$

The values h and dh/dt were calculated at various times during a dynamic run and h was plotted versus rate to determine the intercept H:

$$h = -\frac{1}{k_p} \cdot \frac{dh}{dt} + H \quad \ldots\ldots\ldots\ldots\ldots (14)$$

For the situation when solute permeated the membrane, the method of Elias (23) was found applicable. This method was based on equation (14) and required that the permeation constant should be evaluated with pure solvent on both sides of the membrane by means of the following equation:

$$k_p = \frac{2.303 \log (h_o/h)}{t} \quad \ldots\ldots\ldots\ldots\ldots \quad (15)$$

The average value of the permeation constant was substituted into equation (14) along with rate versus hydraulic head data for an osmotic pressure run. Thus osmotic pressure head may be calculated for each value of hydraulic head.

D. POLYMER FRACTIONATION

A polydisperse polymer sample can be separated into its constituent fractions by fractional precipitation which is based on molecular weight-solubility relationships. The method involves the incremental addition of a miscible non-solvent to a polymer solution which results in the precipitation of fractions in order of decreasing molecular weights (1, 11, 24).

When the polymer solubility is reduced by the addition of a non-solvent a critical solubility is reached as evidenced by the formation of a second precipitate phase. The system then consists of a solution phase of low polymer concentration and a precipitate phase of high polymer concentration. Fractionation is possible because the ratio of the concentrations of high to low molecular weight species is greater in the precipitate than in the dilute solution. This ratio is proportional to an exponential function of the molecular weight and the concentration (25). This equilibrium distribution of molecules causes long chains (higher molecular weight polymer) to collect preferentially in the precipitate. To prevent low molecular weight species from co-precipitating, the volume ratio of dilute to concentrated phases must be kept large. This is usually accomplished by the removal of precipitate. It has been suggested by Flory (26) that the original concentration of the polymer solution expressed as a volume fraction should be considerably less than the ratio of the molar volumes of solvent and polymer.

The solubility of the polymer fractions in the particular system must be sufficiently dependent on the solvent concentration so that an incremental addition of non-solvent precipitates only a fraction of the sample; otherwise, the entire sample tends to precipitate at the same time.

E. VISCOSITY OF DILUTE POLYMER SOLUTIONS

High polymer molecules possess the capacity to greatly increase the viscosity of the liquid in which they are dissolved even at low concentrations (25). The relative increase in viscosity is called the specific viscosity and is defined:

$$\eta_{sp} = \frac{\eta - \eta_o}{\eta_o} \quad \ldots\ldots\ldots\ldots\ldots (16)$$

where η_o is the pure solvent viscosity and η is the viscosity of a polymer solution. The reduced viscosity or viscosity index η_{sp}/c expresses the average contribution of solute molecules to the solution viscosity. The reduced viscosity can be related to concentration by the Huggins' equation (27, 28):

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c \quad \ldots\ldots\ldots\ldots\ldots (17)$$

where k' is Huggins' slope constant characteristic of a given polymer-solvent system. In general, Huggins' constant decreases with increasing solvent power (29).

The limiting viscosity index at infinite dilution, $[\eta]$, is called the intrinsic viscosity and is a measure of the contribution of individual polymer molecules to the viscosity. It is related to the molecular weight by the Staudinger equation:

$$[\eta] = KM \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (18)$$

For a polydisperse fraction M in equation (18) is the viscosity-average molecular weight. However, for fractions which have a low polydispersity, Kraemer and Lansing (26) interpreted M to be the weight-average molecular weight. The Staudinger equation was modified by Mark and Houwink (30) to include an index term:

$$[\eta] = KM^{\alpha} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (19)$$

Values of the constants for various polymer-solvent systems are reported in the literature (30, 31, 32).

DESIGN AND CONSTRUCTION OF APPARATUS

The osmometer constructed for this experiment was designed to include the best features of the instruments previously described. These included all-metal construction, a small internal volume, a simple filling device, provision for capillary level adjustment, and the use of small precision-bore capillary tubing.

The osmometer was constructed as follows: Two matching circular slabs were cut from 316 stainless steel stock. On one of these a circular face 2½" in diameter was machined to a depth of 1/32". On the other slab the annular region around a similar circle was removed to a depth of 1/16" enabling both slabs to fit together. A series of concentric grooves was machined on the face of each slab to a tolerance of 0.001". Details and dimensions are shown in Figure 3.

Stainless steel tubing ⅛" in diameter was silver soldered to the filling holes on the outer edges of the blocks. The bottom tubing was bent as shown and was connected to Whitey OVS2 V-stem valves by means of standard Swagelock fittings. The top tubes were connected in a similar meanner to Whitey ORS2 micro-regulating valves. These served to displace liquid and regulate the capillary meniscus levels. All valves were installed with the exit port on top thus preventing air bubbles from being trapped inside.

The osmotic pressure head differential was measured by means of precision-bore capillary tubing 0.5 mm. I.D. which was connected to the top regulating valves using 1 mm. glass-metal Kovar seals. A cathetometer was used to read the meniscus levels.

The two osmometer blocks were firmly held together by a large C-clamp. This arrangement simplified the installation of membranes. Guide pins were provided to ensure that the grooves were matched during assembly. The osmometer was held in an upright position by a metal support rack fabricated from brass stock.

A filling tube was provided for each liquid chamber and was attached to the valve on the bottom of each block. Filling was accomplished by means of a syringe and an 18 gauge needle. A rubber serum cap was used to make an air tight connection between the syringe and the stainless steel tubing.

A controlled temperature water bath for the osmometer consisted of a glass aquarium insulated on the outside with a $\frac{3}{4}$" layer of styrofoam. Temperature was controlled to $\pm 0.01^{\circ}C$ by means of a Fisher unitized bath control and thermal regulator. Heat was supplied by a 75 watt immersion heater and cooling water was provided through a coil of $\frac{1}{4}$" copper tubing. An electric laboratory stirrer was used to circulate the water in the bath.

Viscosities were measured using Cannon-Fenske capillary tube viscometers. These were maintained at constant temperature in a "Temp Trol" viscosity bath purchased from the Precision Scientific Company.

Fractionation was carried out using standard laboratory glassware. The precipitated fractions were separated out of solution by means of a CENCO HN-S centrifuge equipped with 50 ml. centrifuge tubes. The re-pulped precipitate was later separated from acetone and water by means of a Buchner funnel and filter paper.

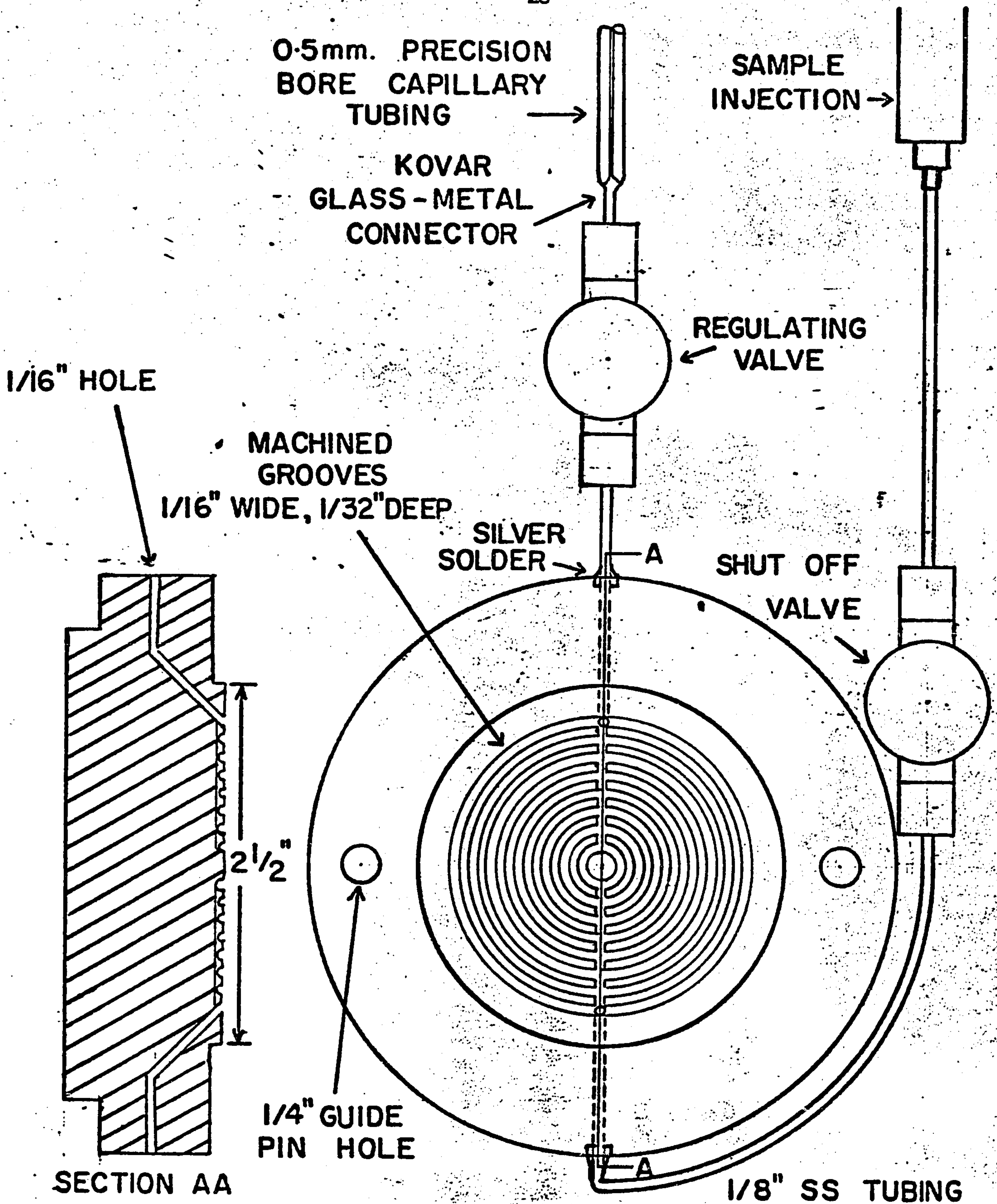

Figure 3 - Detailed drawing of osmometer.

PROPERTIES AND SOURCES OF CHEMICALS AND MATERIALS

The following chemicals and materials were used:

Tetrahydrofuran (THF):

Fisher certified reagent was used and had the following properties:

Viscosity = 0.469 cp.

Density = 0.885 g./ml.

Cyclohexanone:

Fisher purified reagent was used and had the following properties:

Viscosity = 2.020 cp.

Density = 0.947 g./ml.

Ethanol:

Ethanol used was 99% pure and was supplied by Gooderham and Worts Limited.

Acetone:

Acetone used was Fisher certified reagent.

Polyvinyl Chloride:

Samples of Esso PVC grades 353, 363, and 373 were obtained from Imperial Oil Enterprises Limited, Sarnia, Ontario.

Membranes:

Cellulose derivative membranes were obtained from the Schleicher and Schuell Company, N.H. They were 65 mm. in diameter and were of types 07 and 08.

Storage and Conditioning of Membranes:

Membranes were supplied in 20% ethanol and were refrigerated until use. They were conditioned to pure ethanol in a series of solution baths as follows (33). First, they were transferred to a 50-50 mixture of ethanol-water for 2 hours; this mixture was changed to 75-25 ethanol-water for another 2 hours and finally changed to pure ethanol.

Further conditioning to the solvent (THF) was carried out in the osmometer. The reason for this was that THF caused membrane shrinkage. By clamping the membrane between the faces of the osmometer blocks any slight shrinkage that did occur took up the membrane slack and produced a firm diaphragm. The solutions used for conditioning were made up of THF-ethanol in the volume proportions 25-75, 50-50, and 75-25. Each solution was injected by syringe into both chambers of the osmometer for a period of 2 hours. Finally, the chambers were filled with pure THF.

EXPERIMENTAL PROCEDURE

A. OSMOMETER OPERATION

The details of the procedure for installing membranes in the osmometer were as follows. The capillary tubes were loosened and removed to prevent breakage. The grooved faces were moistened with ethanol and a membrane conditioned to ethanol was carefully placed with tongs over the grooves on one of the faces. Immediately, the blocks were clamped together and the assembled instrument was placed in its stand in the temperature bath. Considerable care and practice was required to perform this operation without shearing and buckling the membrane. The membrane was conditioned to THF as outlined in the previous section.

The membrane was tested for leakage by slowly adjusting the meniscus levels independently with the two micro-regulating valves. Membrane stretching often caused both levels to move simultaneously over a distance of 0.5 cm. when one of the levels was rapidly moved. However, if these levels failed to move independently after this, then leakage was suspected between the two chambers of the osmometer. If both levels dropped then a poor seal between the grooved faces and the membranes was indicated and the faces were re-surfaced on the lathe. Failure of the meniscus levels to respond immediately to the valve manipulation indicated the likelihood that a bubble was trapped inside the osmometer. Bubbles were removed by applying a slight suction to the top of the capillaries using a rubber bulb. Such a procedure had been previously used by Immergut and Mark (34).

The procedure for measuring the permeation constant of solvent through the membrane involved timing the rate of change of the hydraulic head across the membrane. Both chambers of the osmometer were initially filled with solvent. It was possible in this way to calculate an actual flow rate of solvent through the membrane for a particular hydraulic head. Permeation constants were calculated for each value of hydraulic head using equation (15).

Thermometric effects were observed in the osmometer by measuring both levels at a given temperature and then raising the temperature slightly. The new levels were used to calculate the thermal sensitivity.

B. SOLUTION PREPARATION

Samples of commercial polyvinyl chloride were dried at 100°C for several hours. Initially, solutions were prepared by weighing small portions of polymer and dissolving them in 100 ml. of tetrahydrofuran. A range of polymer concentrations was required so that weights of diminishing quantities of polymer were used. Each solution was set aside for at least two days to ensure that all the polymer dissolved. Subsequently, a more satisfactory procedure was adopted in which a relatively concentrated solution was prepared (approx. 5 g./l.) from which aliquot portions were simply diluted with solvent to produce the lower concentrations desired.

C. MEASUREMENT OF OSMOTIC PRESSURE

The assembled osmometer was first used to measure osmotic pressures of solutions of Esso 353 grade PVC. The THF was displaced from one chamber of the osmometer with dilute polymer solution using a syringe, care being taken to remove all bubbles.

Various dynamic and static measurements of osmotic pressure were made for comparison and to determine the most practical one for routine PVC analysis. A dynamic response history for the meniscus levels was recorded for flow in both directions through the membrane. A Fuoss-Mead half-sum plot was constructed and the osmotic pressure head was obtained from it. The methods of Bruss and Stross, Philipp, and Elias were also used to estimate the osmotic pressure from the same dynamic response data. Finally, an overnight reading was taken to serve as a static or equilibrium osmotic pressure.

A dynamic method similar to the Bruss and Stross method was devised to give rapid but reliable results utilizing the volume regulating valves of the osmometer. It consisted of measuring the rate of change of the hydraulic head during specified time intervals for only a few values of hydraulic head. To do this, the levels were pre-set slightly above or below the expected osmotic pressure head. After a given time interval (usually 10 minutes) the rate of change was calculated in conjunction with the average hydraulic head. Equilibrium was then approached from the opposite direction but closer to the expected osmotic pressure head. This method was repeated about five times and a least mean squares fit of the data was used to obtain the equilibrium osmotic pressure head.

A membrane with a slight asymmetry pressure was chosen and separate solutions of Esso 363 grade PVC were analysed using the method of Bruss and Stross. Values of osmotic pressure head were also calculated by the method of Philipp. The asymmetry pressure was subtracted from the osmotic pressure to obtain a corrected reading. The effect and importance of making such a correction is shown in the results.

D. POLYMER FRACTIONATION

A sample of Esso 373 grade PVC was separated into its constituent fractions by fractional precipitation by adding a non-solvent to a polymer solution.

About 5 grams of the polymer was moistened with 50 ml. of acetone to aid solution followed by 100 ml. of cyclohexanone. Following complete solution the mixture was diluted with a further 100 ml. of acetone. This mixture was placed in a beaker and with vigorous agitation was titrated with a precipitant solution consisting of 40 volume % ethanol, 40 volume % water, and 20 volume % acetone. Upon first signs of a precipitate the mixture was centrifuged, the precipitate removed, and subsequently washed in acetone. The wash liquid was combined with the original filtrate which was titrated further. The gel-like precipitate was re-pulped in excess acetone and precipitated out with a 50-50 mixture of ethanol and water. It was then filtered out on a Buchner funnel and dried at 100°C to constant weight. The process was repeated with the original filtrate until five fractions were obtained.

Each fraction was dissolved in THF and analysed by osmometry to obtain the number-average molecular weight.

E. INTRINSIC VISCOSITY

Intrinsic viscosities were obtained for each fraction of Esso 373 grade PVC and also for the other unfractionated samples of Esso 353 and Esso 363. A calibrated viscometer was thoroughly cleaned and used to measure the viscosity of pure solvent (THF) at 25°C. Temperature was controlled to ± 0.05°C. The viscosities of various solutions of each fraction or grade were also measured and the reduced specific viscosity of each solution was calculated. A least mean squares fit was used to linearly extrapolate to zero concentration for the determination of the intrinsic viscosity. The weight-average molecular weight of each sample was calculated by means of correlations in the literature.

EXPERIMENTAL RESULTS

This section includes significant and illustrative results obtained in the course of this research. Accompanying each section is an explanation concerning the treatment of the data. Detailed results and calculations are included in the Appendices.

A. PERMEATION CONSTANTS

Permeation constants were measured for flow of solvent through various membranes. Experiments were also carried out with flow through the membranes in both directions to determine the possible effects of membrane asymmetry.

RUN NO.	MEMBRANE TYPE	SOLVENT	SOLVENT VISCOSITY (cp.)	PERMEATION CONSTANTS (cm./(min.)(cm. of solvent head)) A	B
M-1	08	THF	0.469	0.0460	0.0452
M-2	07	THF	0.469	0.1416	0.1580
M-3	08	cyclohexanone	2.020	0.00383	
M-4	08	THF	0.469	0.0358 - 0.0477	0.0456 - 0.0379

Table 1 - Permeation constants for various membranes.

Notes: (a) A refers to flow through the membrane in one direction while B refers to flow in the opposite direction.

(b) The membrane used in Run M-4 had an asymmetry pressure head of 0.350 cm. on side B.

(c) Actual data is given in Appendix B.

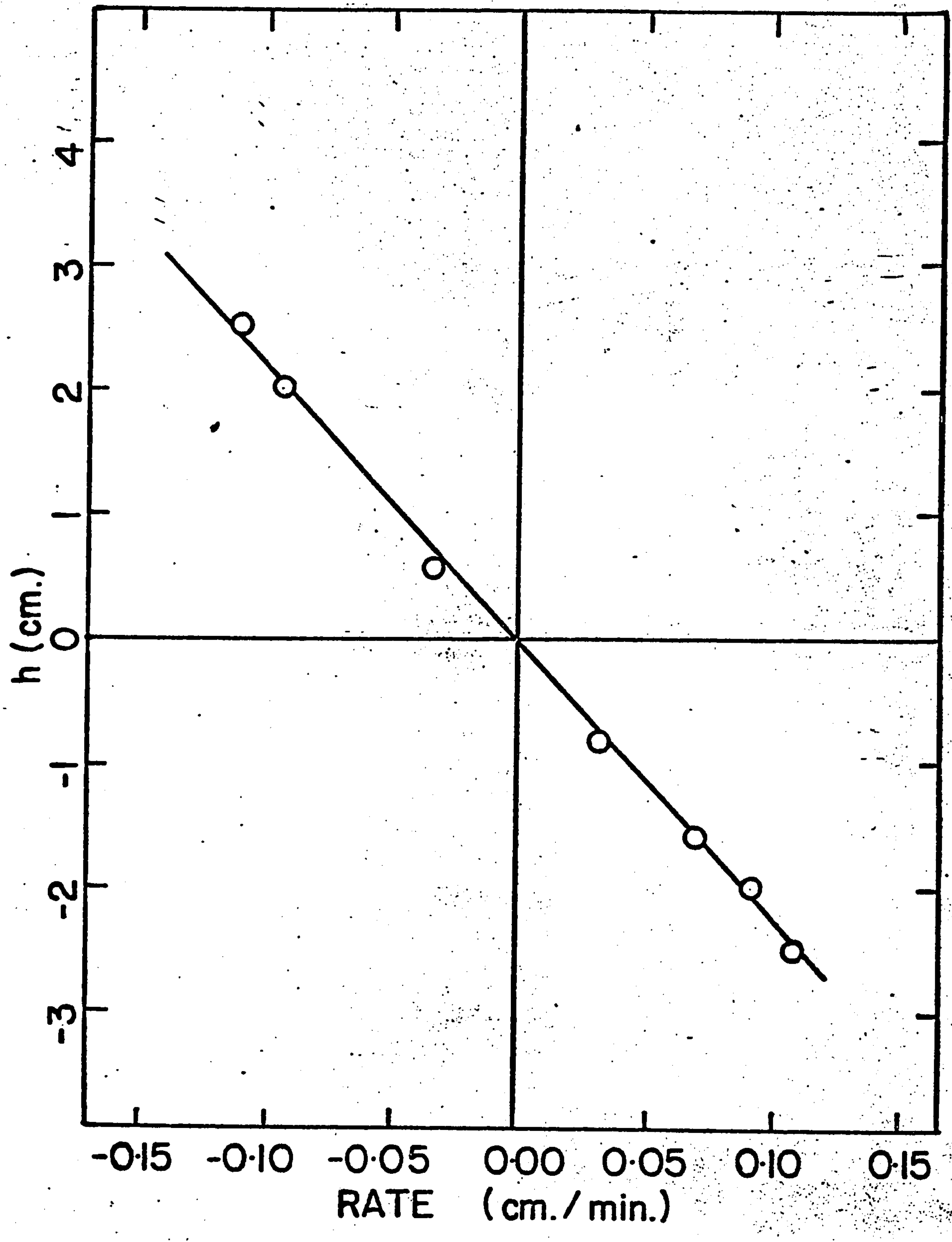

Figure 4 - Bruss and Stross plot for Run M-1.

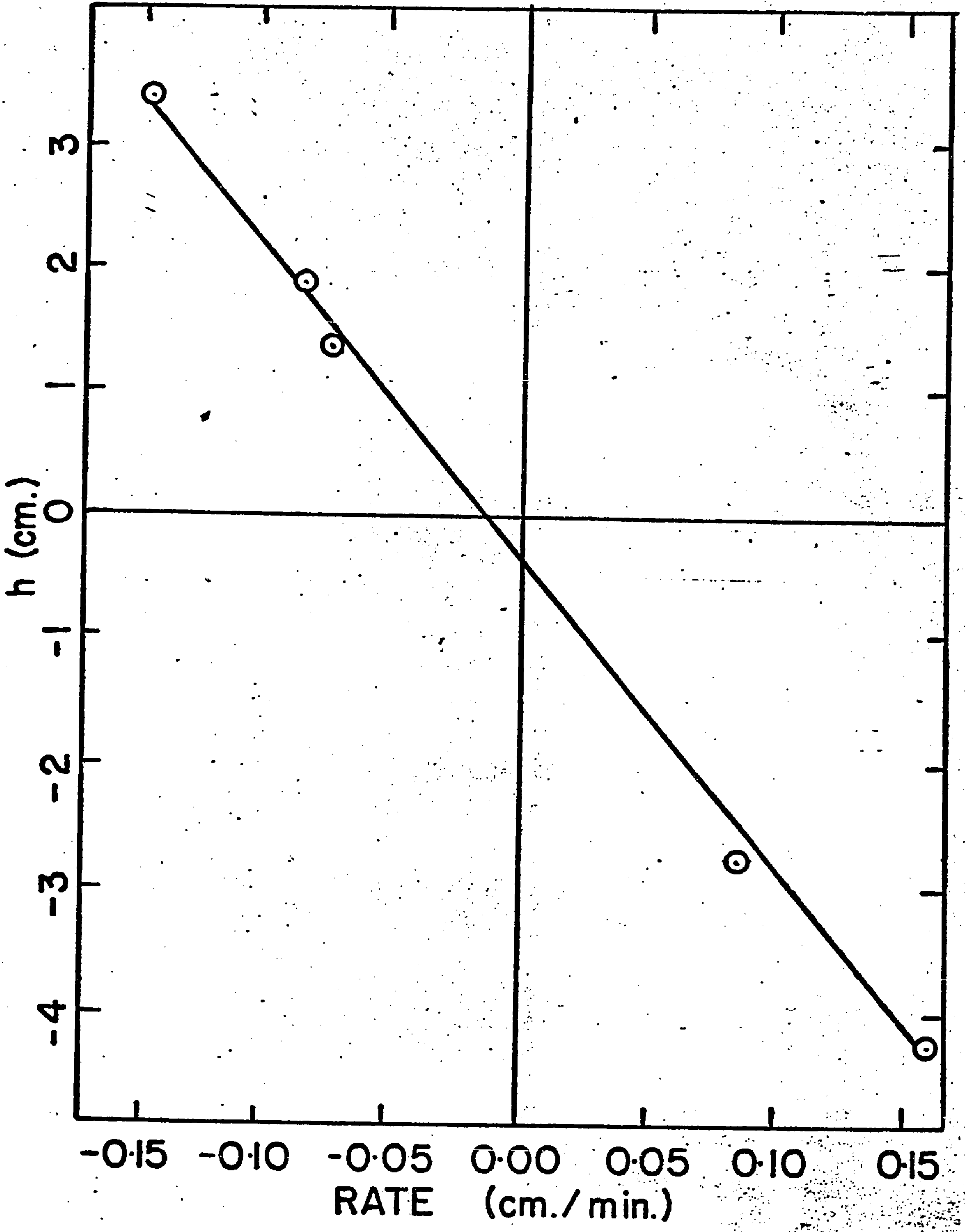

Figure 5 - Bruss and Stross plot for Run M-4.

The permeation constants for each membrane were calculated for each hydraulic head measured. The results were consistent for Run M-1 and the permeation constant did not vary with flow rate or with direction of flow. A Bruss and Stross plot (Figure 4) was constructed from the data of Run M-1 and a permeation constant of 0.0445 cm./(min.)(cm. of solvent head) was obtained from the slope using the method of least mean squares. An apparent slight asymmetry pressure was also observed from the plot but this small deviation was considered to be within experimental error.

Results based on the method of Elias for Run M-4 were not consistent because the expression for the permeation constant was developed from the assumption that both levels correspond at equilibrium. From the dynamic response data for the difference in levels with time an asymmetry pressure of 0.350 was calculated. As an alternative method for determining the asymmetry pressure a Bruss and Stross plot was constructed and a permeation constant of 0.0395 cm./(min.)(cm. of solvent head) was calculated from the slope. An asymmetry pressure of 0.373 cm. was obtained from the intercept.

The permeation constants for Run M-2 and Run M-3 were obtained by the method of Elias and were quite consistent. The 07 membrane used for Run M-2 had a higher permeation constant than the 08 membrane. When cyclohexanone, a more viscous solvent, was used a much lower permeation constant was obtained. Possible reasons for this will be discussed later.

B. COMPARISON OF VARIOUS METHODS FOR MEASURING OSMOTIC PRESSURE

Identical solutions of Esso 353 PVC ranging in concentration from 0.344 to 3.464 g./l. were analysed by various methods to determine the osmotic pressure. The reduced osmotic pressure head was plotted versus concentration for each method and a least mean squares fit was used to determine the number-average molecular weight. The methods were then compared on the basis of standard deviation of the respective reduced osmotic pressures except for the Elias and Philipp methods which did not give consistent results. These latter two gave only an approximation of the osmotic pressure head. The dynamic response curves and Bruss and Stross plot are included from the analysis of the most dilute solution (0.344 g./l.).

METHOD	NO. OF MEASUREMENTS	TIME REQUIRED PER MEASUREMENT (hours)	SLOPE (cm. l^2/g^2)	INTERCEPT (cm.l./g.)	STANDARD DEVIATION	$\overline{M}_n$ (g./g. mole)
Static	5	5	0.0352	0.898	0.0153	31,800
Bruss and Stross (including modified)	6	2	0.0542	0.8133	0.0339	35,100
Fuoss-Mead	5	2	0.0481	0.8384	0.0382	34,000

Table 2 - Comparison of methods for measuring osmotic pressure in terms of speed and standard deviation.

CONC. (g./l.)	H (cm.)	H/c (cm. l./g.)
0.344	0.310	0.901
0.484	0.452	0.934
1.250	1.170	0.937
2.126	2.019	0.953
3.464	3.570	1.030

Table 3 - Readings obtained from static method.

CONC. (g./l.)	H (cm.)	H/c (cm. l./g.)
0.344	0.301	0.876
0.484	0.393	0.812
1.250	1.023	0.818
1.283	1.195	0.931
2.126	1.940	0.913
3.464	3.510	1.015

Table 4 - Readings obtained from Bruss and Stross method.

CONC. (g./l.)	H (cm.)	H/c (cm. l./g.)
0.344	0.305	0.886
0.484	0.430	0.888
1.250	1.030	0.824
2.126	1.980	0.933
3.464	3.570	1.030

Table 5 - Readings obtained from Fuoss-Mead method.

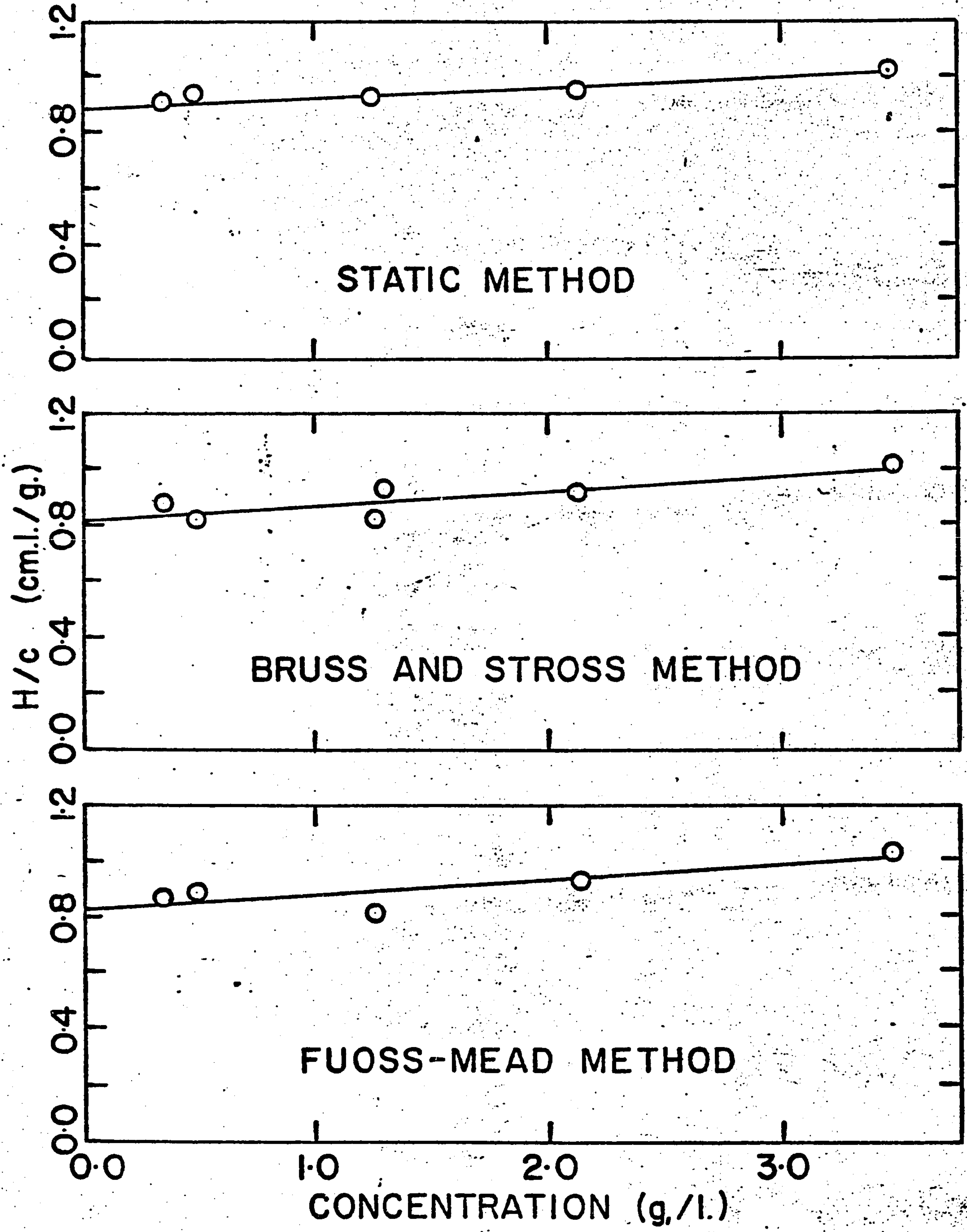

Figure 6 - Reduced osmotic pressure head plots for various methods.

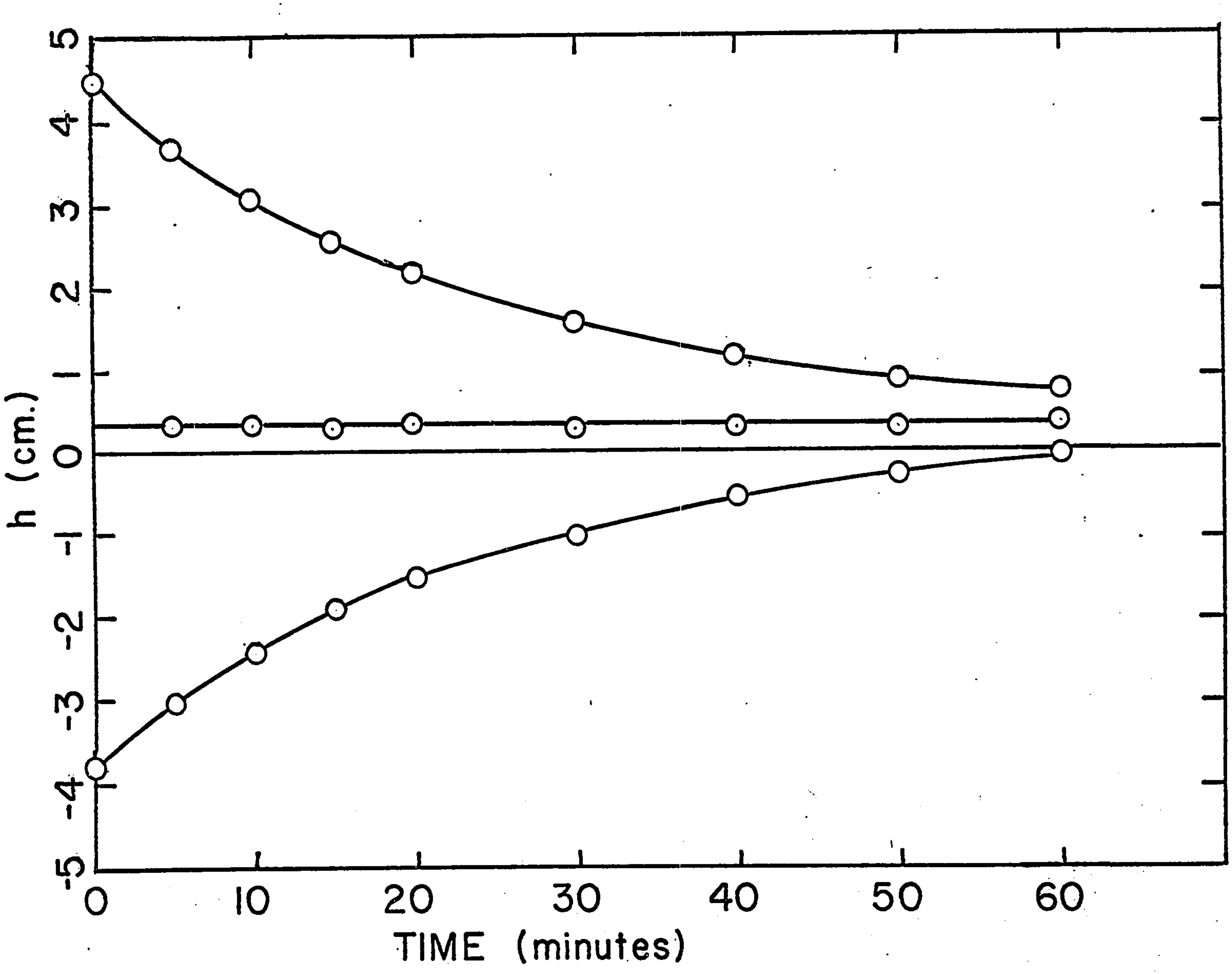

Figure 7 - Dynamic response curves for run 353-1 (solution concentration -0.344 g./l.)

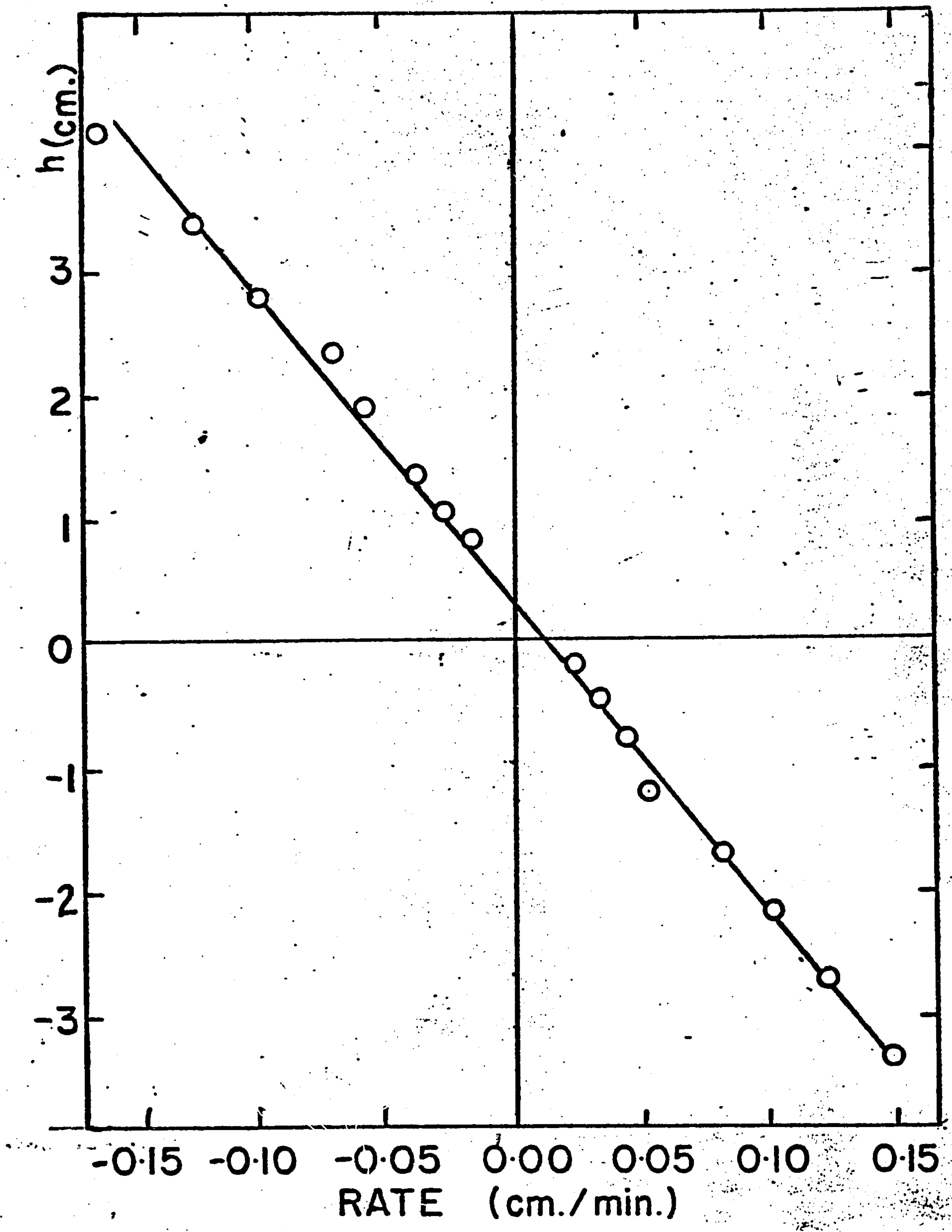

Figure 8 - Bruss and Stross plot for run 353-1 (solution concentration - 0.344 g./l.)

		OSMOTIC PRESSURE METHOD			
SOLUTION CONCENTRATION (g./l.)	STATIC READING	BRUSS AND STROSS	FUOSS-MEAD	ELIAS	PHILIPP
0.344	0.310	0.301	0.305	0.105 - 0.522	0.139 - 0.493
0.484	0.452	0.393	0.430	0.324 - 0.712	0.113 - 0.809
1.250	1.170	1.023	1.030	0.815 - 1.395	0.435 - 1.596
1.283		1.195			
2.126	2.019	1.940	1.980	1.889 - 2.262	2.447
3.464	3.570	3.510	3.570	3.335 - 3.795	3.330 - 4.020

Table 6 - Comparison of actual readings for each method.

Note: Dynamic readings were taken in approaching equilibrium from both directions. See Appendix C.

C. ANALYSIS USING AN ASYMMETRIC MEMBRANE

A membrane found to exert an asymmetry pressure on one side (see section A) was used to determine the osmotic pressure of two separate solutions of Esso 363 grade PVC. Each solution was injected into the osmometer chamber on the side of the membrane with the positive asymmetry pressure. The levels were adjusted to correspond so that equilibrium was approached in the positive direction (flow of solvent into solution). A dynamic response history of the levels was recorded and analysed by the method of Bruss and Stross. The method of Philipp was also used as a consistency check.

CONC. (g./l.)	MEASURED OSMOTIC PRESSURE HEAD (cm.)		H/c (cm.l./g.)	H (corrected)	H/c (corrected)
	BRUSS AND STROSS	PHILIPP			
1.554	1.261	1.220 - 1.395	0.813	1.051	0.677
2.333	1.752	1.644 - 1.893	0.752	1.542	0.664

Table 7 - Osmotic pressure data for Esso 363 PVC.

Note: Asymmetry pressure head = 0.21 cm. on solution side.

As seen in Table 7 both methods gave approximately the same osmotic pressures for a particular solution illustrating that the asymmetry did not affect the dynamics of flow through the membrane. To obtain consistent values of H/c for the two solutions it was first necessary to subtract the asymmetry pressure head from the osmotic pressure head.

D. INTRINSIC VISCOSITY

Solution viscosities of the same grades of PVC used in the osmotic pressure determinations were measured in THF at 25°C. The solution concentrations covered the same general range as those used for osmotic pressure measurements. Reduced specific viscosities were plotted versus concentration for each grade and the intrinsic viscosity was calculated by the method of least mean squares. Huggins' constant was calculated from the relationship:

$$k' = \text{SLOPE}/[\eta]^2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (20)$$

which shows the variation of slope with intrinsic viscosity. The literature value obtained by Moore and Hutchinson (29) for narrow fractions is 0.37. The weight-average molecular weight was assumed equivalent to the viscosity-average molecular weight and was calculated from the following relationship:

$$\bar{M}_w = \left[\frac{[\eta]}{1.63 \times 10^{-5}}\right]^{1/0.766} \qquad \ldots\ldots\ldots\ldots\ldots \quad (21)$$

PVC GRADE	(l./g.)	SLOPE (l^2/g^2)	HUGGINS' CONSTANT	$\bar{M}_w$ (g./g. mole)
353	0.0669	0.0015	0.334	52,400
363	0.0832	0.0027	0.389	69,000
373	0.1174	0.0054	0.391	112,000

Table 8 - Intrinsic viscosity data for various PVC grades.

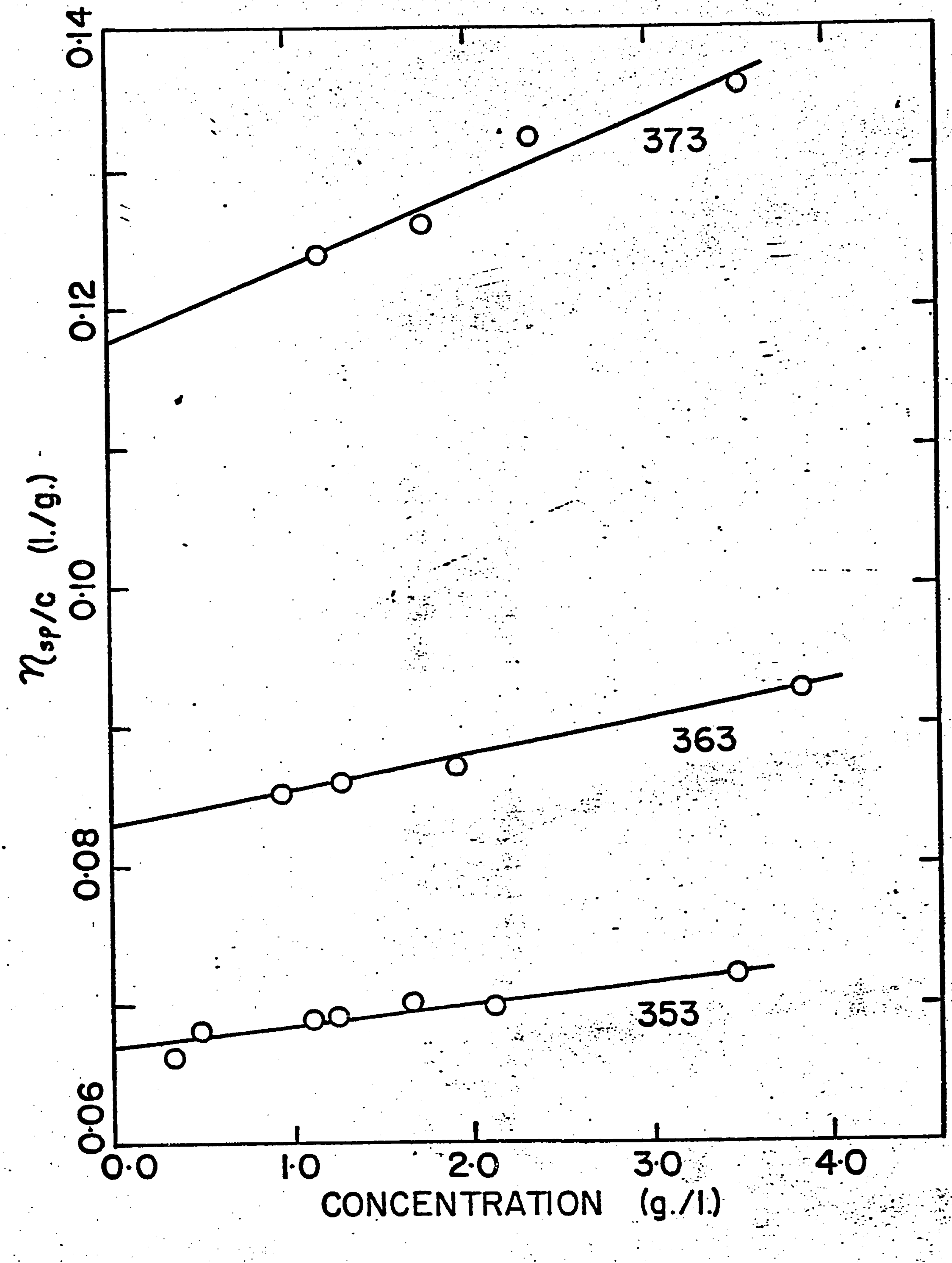

Figure 9 - Viscosity slopes for various grades of PVC.

E. FRACTIONATION OF POLYVINYL CHLORIDE

A sample of Esso 373 PVC was fractionated into 5 constituent fractions as outlined in the procedure. The weight of each fraction was expressed as a percentage of the total weight of polymer fractionated and was plotted against the cumulative volume of precipitant used. Results were as follows:

Total weight of polymer = 4.9455 g.

FRACTION	TITRE OF PRECIPITANT (ml.)	WEIGHT OF FRACTION (g.)	CUMULATIVE WEIGHT PERCENT RECOVERED
1	25.0	0.2978	6.03
2	28.5	0.3825	13.75
3	32.0	2.4265	62.90
4	37.0	1.2754	88.80
5	47.0	0.2689	94.20

Table 9 - Fractionation of Esso 373 grade PVC.

It can be seen that approximately 6% of the total weight of polymer was not recovered. This loss can be divided among all the fractions in proportion to their weights by simply dividing the percentages in Table 9 by the total percentage recovered.

The accompanying graph (Figure 10) shows a rather sharp separation occurring in the intermediate range where the amount of polymer in solution is extremely sensitive to the addition of a small amount of precipitant.

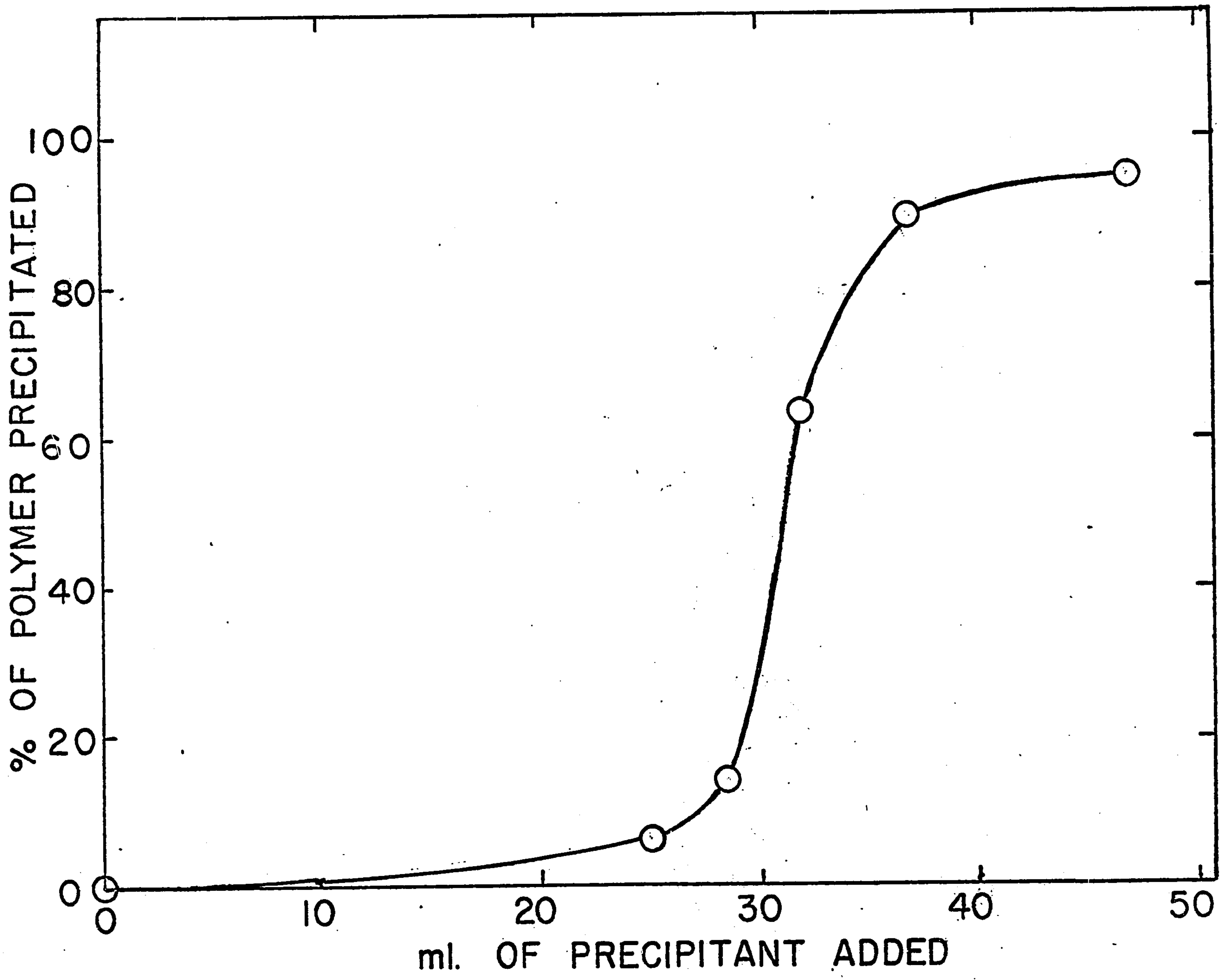

Figure 10 - Fractionation curve for Esso 373 PVC.

Portions of each fraction were dissolved in THF and diluted to produce concentrations ranging from 0.55 to 4.88 g./l. The higher molecular weight fractions were generally more difficult to dissolve so that it was found necessary to prepare concentrations of less than 5 g./l. for the most concentrated solution. The osmotic pressure head and viscosity were measured for each solution. Reduced plots for both these properties were constructed and fitted by the method of least mean squares. The number-average and weight-average molecular weights were calculated as previously outlined. In Table 10 the total weight of each fraction is listed. The weight of the composite sample shown is the sum of the weights of all the fractions. The number of moles of each fraction is simply the weight divided by the number-average molecular weight and is based on the assumption that the molecular weight distribution of each fraction is symmetric about its number-average molecular weight.

The results for the individual fractions were used to calculate the number-average and weight-average molecular weights of the composite sample according to equations (1) and (2). These were as follows:

$$\bar{M}_n = 76{,}100 \text{ g./g. mole.}$$

$$\bar{M}_w = 115{,}000 \text{ g./g. mole.}$$

Details of these calculations are shown in Appendix G.

A fractionation curve based on number-average molecular weights is shown in Figure 13. It can be seen that molecular weights ranging from 70,000 to 90,000 constitute most of the sample in terms of moles. This also explains the sharp separation in Figure 10; molecules of similar molecular weight have similar solubilities.

FRACTION	WEIGHT	$\overline{M}_n$ (g./g. mole)	g. Moles x 10^3	$[\eta]$ (l./g.)	$\overline{M}_w$ (g./g. mole)	$\overline{M}_w/\overline{M}_n$
1	0.2978	137,500	0.00216	0.1466	146,000	1.060
2	0.3825	110,800	0.00346	0.1410	136,000	1.229
3	2.4265	92,300	0.0263	0.1335	128,000	1.384
4	1.2754	62,600	0.0204	0.1039	95,400	1.521
5	0.2689	30,400	0.00885	0.0548	40,200	1.322
COMPOSITE 373	4.6511	79,800	0.06118	0.1174	112,000	1.405

Table 10 - Analysis of fractions recovered during fractionation.

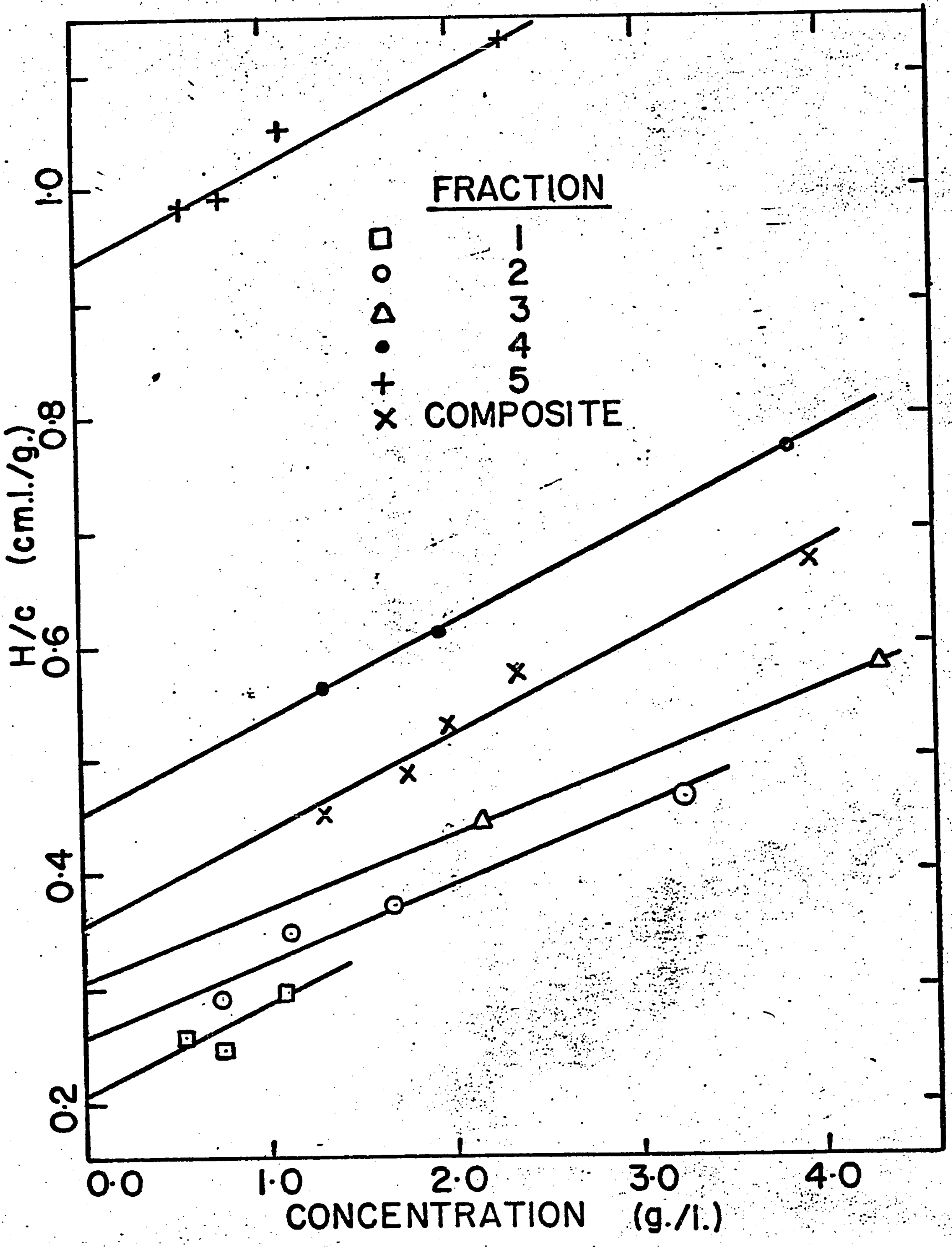

Figure 11 - Reduced osmotic pressure head plots for 373 PVC and its fractions.

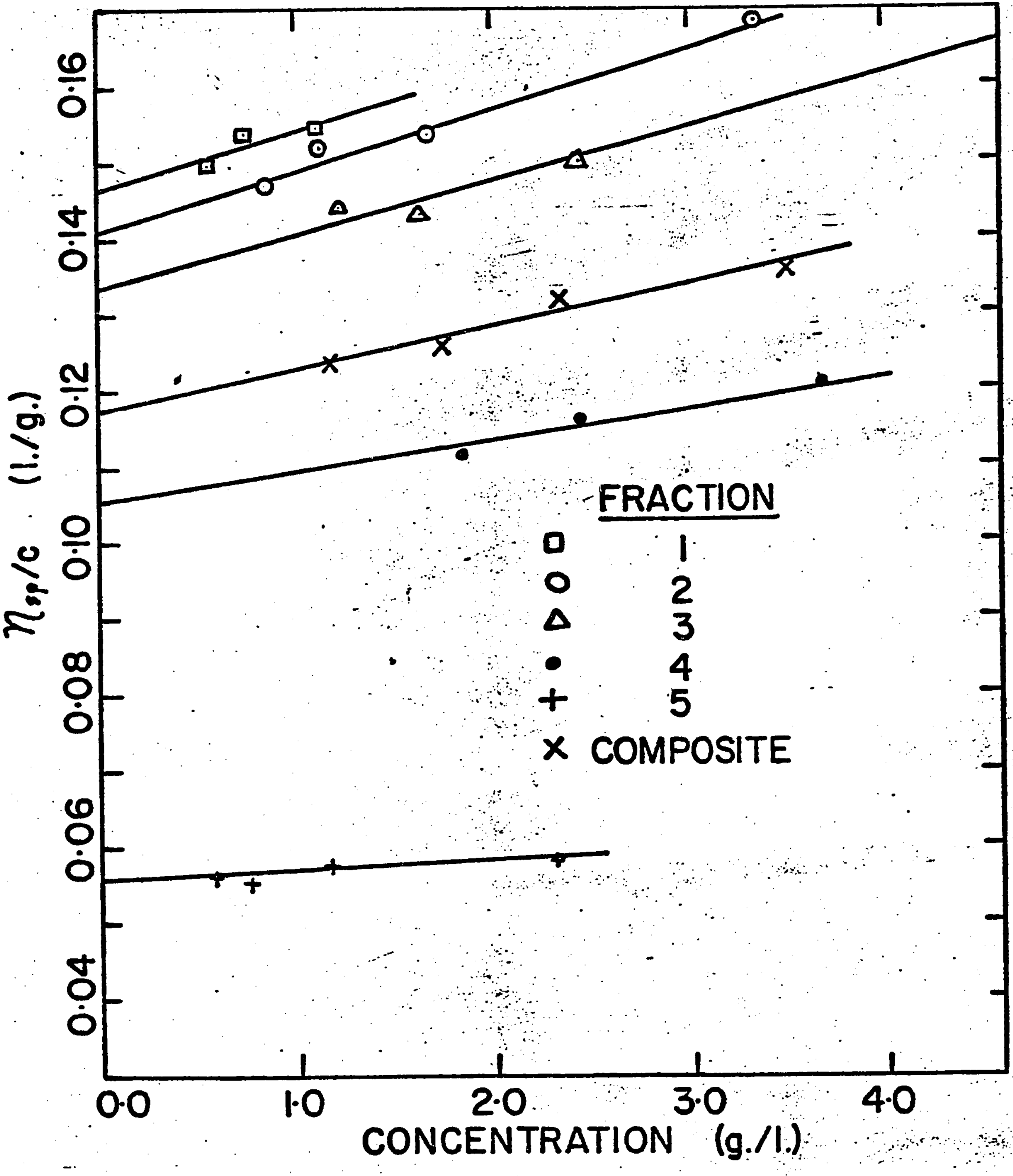

Figure 12 - Viscosity plots for 373 PVC and its fractions.

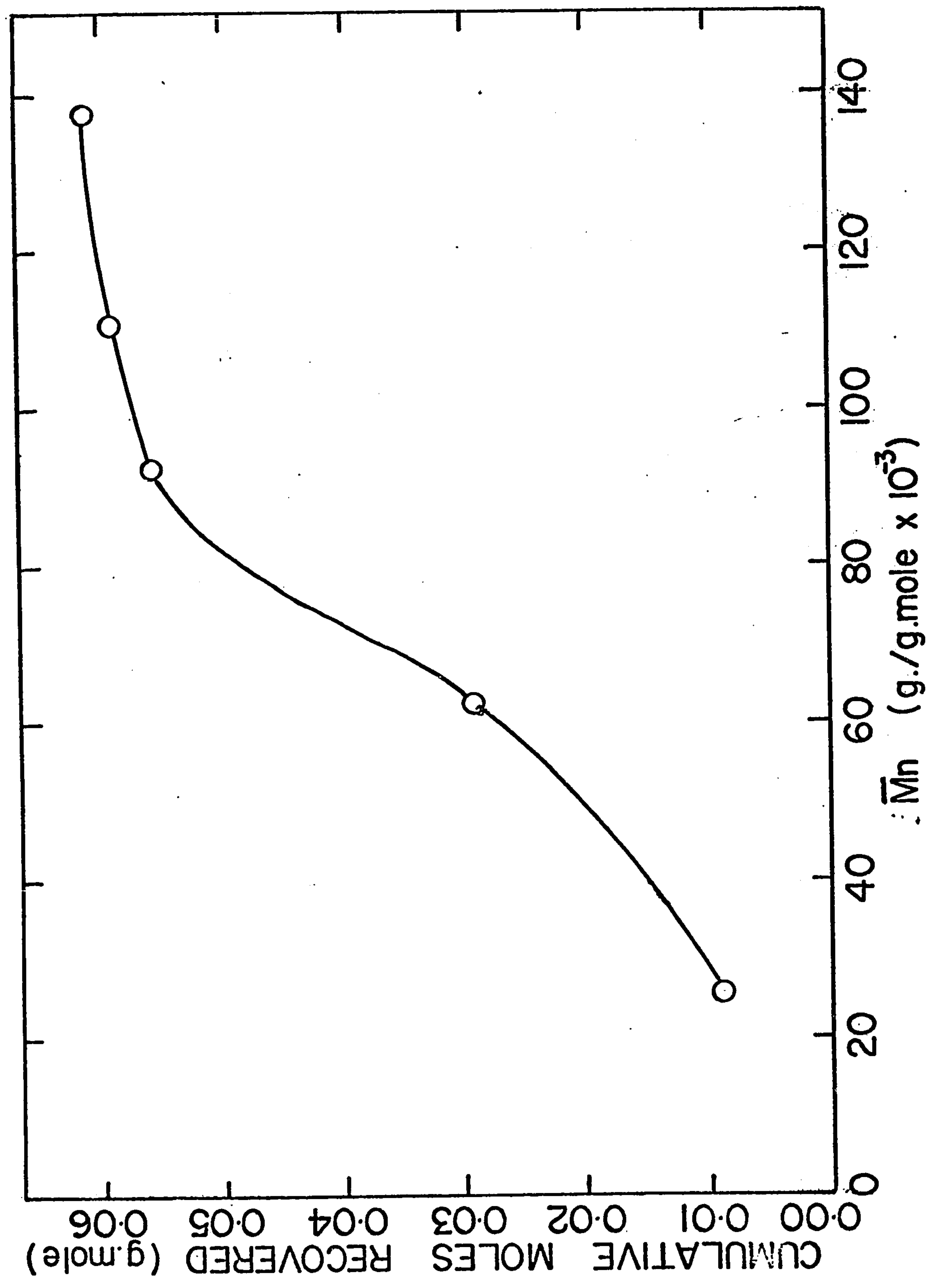

Figure 13 - Fractionation curve based on number-average molecular weights.

Fig[illegible] - [illegible] - [illegible] curve based on number-average molec[illegible] weights.

A polymer sample usually contains a wide range of molecular weights. If ultimate fractionation were possible, a sample could be separated into a large number of fractions such that each consists of material having only one molecular weight. It would then be possible to obtain distributions of the number of molecules of each molecular weight and also of the mass of molecules of each molecular weight. Number-average and weight-average molecular weights could then be calculated in the classical sense.

In actual practice perfect fractionation is impossible and the method of obtaining a molecular weight distribution from a knowledge of the fractions of a polymer is more complicated. The fractions are polydisperse and overlap one another in molecular weight ranges. Also it is very difficult to control the size of the fractions during the addition of non-solvent and the amounts in the fractions are generally different. Finally, during a fractionating process losses of polymer are incurred, the molecular weight range of which is difficult to estimate. For these reasons it is difficult to reconstruct the actual molecular weight distribution from a limited knowledge of the molecular weight of the fractions.

Some attempt to reconstruct the original molecular weight distribution from the molecular weights of the fractions has been made in this research. It was considered that the fractions had similar and symmetrical molecular weight distributions even though the ranges overlapped one another. It was further considered that a measure of the polydispersity for each fraction was the difference between the weight-average and number-average molecular weights of that fraction. Because the weight of each fraction was known along with the average molecular weights it was possible to define a molar distribution function as follows:

$$\Phi = \frac{w_i}{\overline{M}_{ni}(\log \overline{M}_{wi} - \log \overline{M}_{ni})} \quad \ldots\ldots\ldots\ldots \quad (22)$$

The subscript i identifies each fraction. The use of this function assumes that the molecular weight distribution is symmetric about the number-average molecular weight. When ϕ is plotted against the logarithm of the number-average molecular weight a distribution curve is obtained, the area under which represents the number of moles. The choice for using a logarithmic interval of molecular weight instead of a linear one was for convenience only. It is worth noting that the distribution function can be evaluated for every fraction regardless of its size or whether there is overlapping between the fractions.

A weight distribution function can be defined as follows:

$$\Theta = \frac{w_i}{(\log \overline{M}_{wi} - \log \overline{M}_{ni})} \quad \ldots\ldots\ldots\ldots \quad (23)$$

When this function is plotted against the logarithm of the weight-average molecular weight, a distribution curve is obtained. The area under this distribution curve represents the weight of the polymer.

FRACTION	WEIGHT (g.)	$\overline{M}_{n_i}$ (g./g. mole)	$\overline{M}_{w_i}$ (g./g. mole)	$(\log \overline{M}_{w_i} - \log \overline{M}_{n_i})$	ϕ (g. moles x 10^4)	θ (g.)
1	0.2978	137,500	146,000	0.0260	0.830	11.43
2	0.3825	110,800	136,000	0.0891	0.389	4.29
3	2.4265	92,300	128,000	0.1420	1.855	17.10
4	1.2754	62,600	95,400	0.2830	0.722	4.51
5	0.2689	30,400	40,200	0.1214	0.728	2.21

Table 11 - Molecular weight distribution functions.

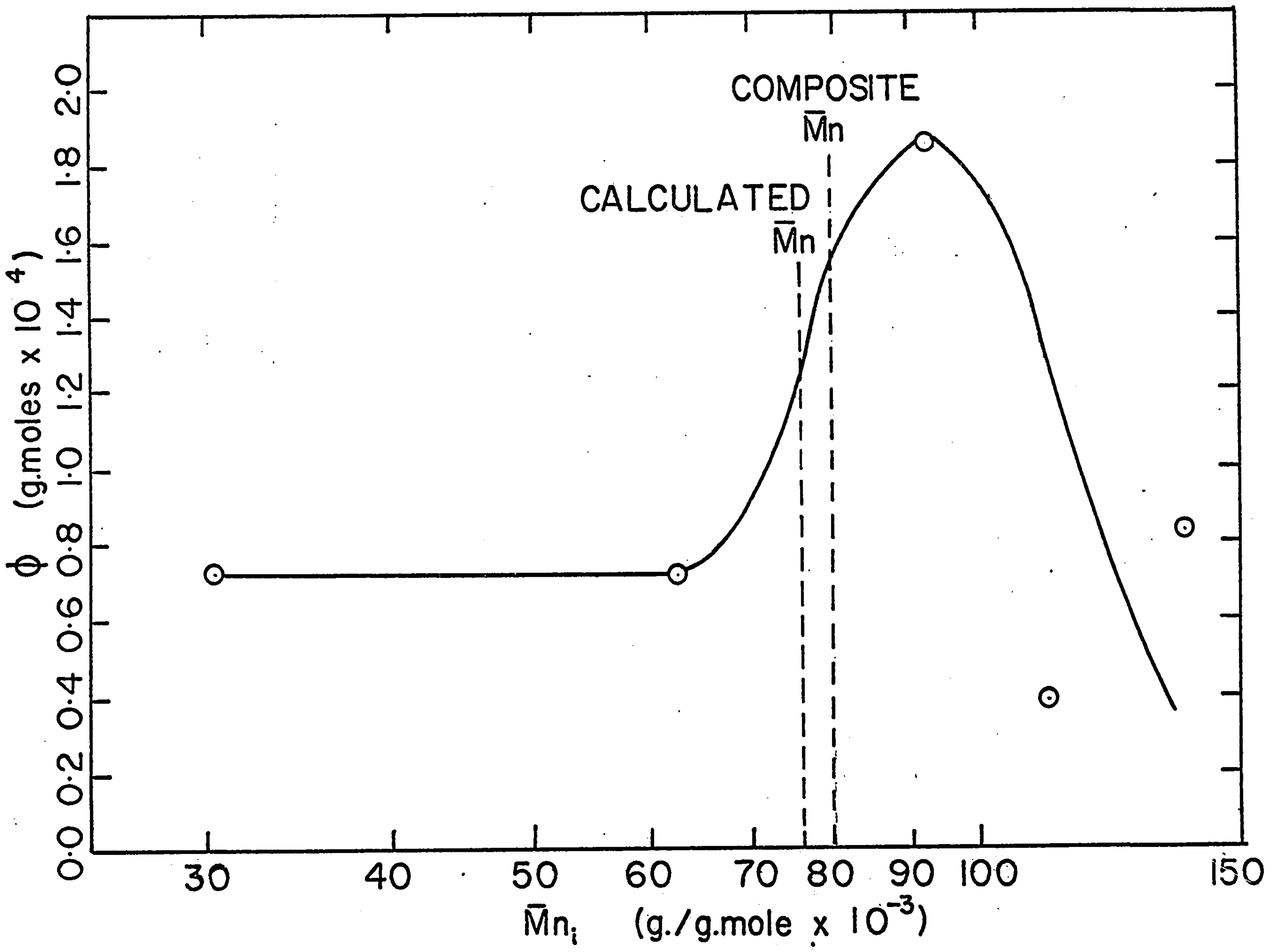

Figure 14 - Molar distribution of molecular weights in 373 grade PVC.

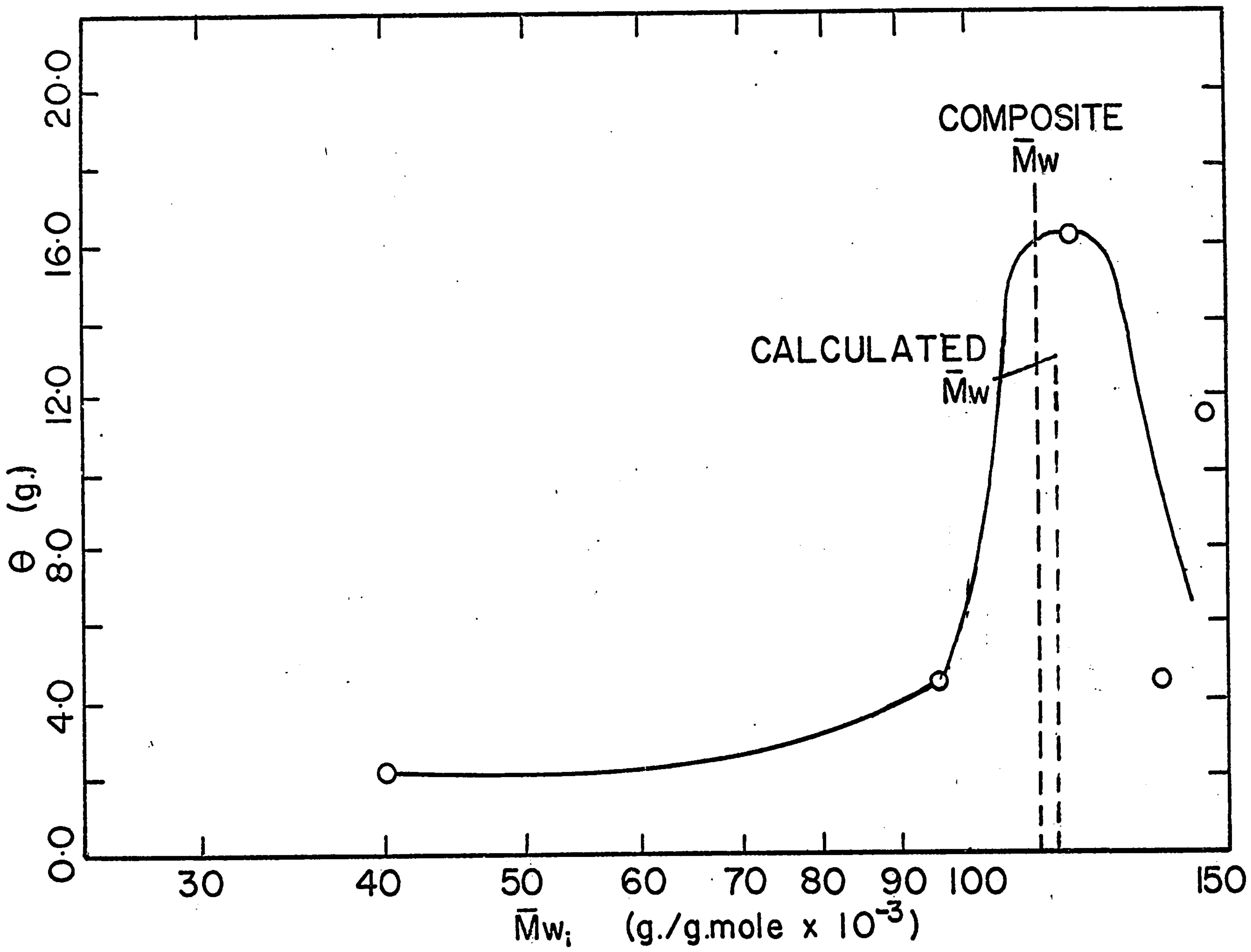

Figure 15 - Weight distribution of molecular weights in 373 grade PVC.

DISCUSSION

A. OSMOTIC PRESSURE MEASUREMENTS

The osmometer constructed for this research was found very satisfactory. The features which were particularly useful were the ease of assembly, the filling device, and the simple adjustment of meniscus levels by volumetric displacement. The two separate chambers used for solution and solvent enabled the osmometer to be placed directly into a water bath without being immersed in excess solvent. The escape of toxic solvent vapours into the atmosphere was thereby prevented. The matching chambers and capillaries reduced the net effect of small temperature fluctuations because both levels changed simultaneously.

Flow measurements were first carried out using pure THF on both sides of the membrane. The permeation constant for flow through a Schleicher and Schuell 08 membrane was calculated by two different methods and for flow in both directions. It was expressed in terms of flow/head of solvent, and consistent results were obtained in each case. When comparing measurements made in different osmometers it is necessary to express the permeation constant in terms of capillary area and exposed membrane area according to equation (10).

The flow rate through an asymmetric 08 membrane was measured and the permeation constant, determined by the method of Bruss and Stross, was found to agree with the previous results for a normal membrane when due allowance was made for the membrane asymmetry. The linear (least mean square) extrapolation of the flow rate-hydraulic head relationship to zero flow could be reliably used to establish the presence of an asymmetry pressure and to measure its magnitude. Thus it was possible to evaluate the asymmetry pressure without actually waiting until an equilibrium hydraulic difference had been reached.

When a coarse 07 membrane was used the permeation constant increased by more than three times its previous value. Since this membrane was chemically the same as the 08 type and since the same solvent was used, the increase in the permeation constant can be attributed to a larger pore radius in equation (10), a smaller membrane thickness or a combination of both. This explains also why the 07 membrane is recommended by the manufacturer for use only with higher polymer fractions (33). Otherwise, low molecular weight polymer might permeate through the membrane.

When cyclohexanone was used as a solvent the permeation constant of a 08 membrane decreased to less than 1/10 its value with THF solvent. The viscosity of cyclohexanone was measured to be only about four times that of THF and the solvent densities were approximately the same. Changes in membrane porosity, pore size and thickness in equation (10) must have accounted for most of the change in permeation constant for the two solvents. This suggests that the pore structure of the membrane was altered by the use of a different solvent. The use of cyclohexanone with a 08 membrane resulted in a lower permeation constant possibly because all the pores did not remain open. It has been reported that for a membrane to be permeated by the solvent the solvent must swell the membrane to keep the pores open for flow (17).

Osmotic pressure heads of various solutions were determined by utilizing dynamic readings. The static (equilibrium) readings taken after 5 hours produced little scatter on a reduced osmotic pressure plot but the measurements were excessively time consuming.

Of the dynamic methods employed the Bruss and Stross method was by far the simplest and the results compared favourably with those of the static method. Because the capillary tubes were exposed to the atmosphere, slight ambient temperature fluctuations caused the levels to change making it necessary to read both levels. In this way a modified Bruss and Stross method was adapted; the conventional method involved directly timing the movement of one of the levels between two fixed positions. The advantage of the modified method was that no continuous record of dynamic readings was required. This was because the design of the osmometer permitted the adjustment of levels to any desired position. The osmotic pressure head was calculated by the method of least mean squares and was based on only five rate measurements all of which could be taken in less than one hour. This method produced results which were within ± 0.03 cm. of the equilibrium solvent head.

The methods of Philipp and Elias were found useful only for predicting osmotic pressure head in conjunction with other dynamic methods. A disadvantage was that calculated values varied with position on the dynamic response curve. If either of the methods are to be comparable to the Bruss and Stross dynamic method, some averaging procedure must be incorporated to allow for minor reading errors.

The Fuoss-Mead method required a continuous record of dynamic readings for both positive and negative approaches to equilibrium. The task of taking readings was time consuming and tedious. The choice of initial levels required some prior knowledge of the expected osmotic pressure head and for this reason the method was not readily adaptable for routine use.

Reduced osmotic pressure head plots all had positive slopes which indicated a positive deviation from ideal behavior at finite concentrations. A positive slope can be attributed to a negative heat of solution and an appreciable entropy contribution from polymer-solvent interaction (12). Such deviations from ideal solution behavior are almost invariably observed.

B. INTRINSIC VISCOSITY

The viscosity of a polymer solution is a function of the number of particles in solution and the degree of interaction between them. Solute particles hinder the relative movement of solvent molecules and in this way contribute to an increase in viscosity. Viscosity plots for the various grades of PVC tested in this research had positive slopes which increased with increasing molecular weight. The slope of such a plot is probably the result of solute-solute interaction at finite concentrations. The interacting solute molecules affect the solvent molecules around them and increase the average solution viscosity. Larger polymer molecules having undergone a higher conversion are more likely to be cross-linked and because they interact more than linear molecules, they affect the solution viscosity more than lower molecular weight polymers.

For a particular polymer chain-length the degree of molecular interaction in solution is dependent on the solvent used. Good solvents are effective in reducing solute agglomeration and for this reason the slope on a reduced specific viscosity plot is lower when a good solvent is used. This explains why Huggins' constant varies with solvent power. Huggins' constants obtained in this experiment varied from 0.33 to 0.39 and agreed well with the literature value of 0.37 for PVC in THF.

The variation of the viscosity slope with molecular weight is greatest for rigid rod-shaped molecules and the constant "α" in the Mark-Houwink equation has a maximum value of 2 (35). A minimum value for "α" is obtained for perfectly flexible polymer chains. Deviations from the Mark-Houwink equation have been observed in high molecular weight fractions (32). A possible explanation is that high molecular weight fractions sometimes contain an appreciable number of long-branched molecules and so have a low solution viscosity for their molecular weight. Such long molecules do not hinder the movement of solvent molecules as much as more complex molecules or a greater number of smaller molecules.

C. MOLECULAR WEIGHT DISTRIBUTION

The number-average molecular weight of Esso 373 grade PVC based on the analysis of constituent fractions using equation (1) was found to agree well with that obtained by osmometry for the composite sample. The values were 76,100, and 79,800 g./g. mole respectively.

The weight-average molecular weight based on the individual fractions was obtained by assuming the weight distribution of each fraction to be symmetric about its weight-average molecular weight. The individual weight-averages were substituted into equation (2) and $\overline{M}_w$ was calculated to be 115,000. This compared favourably with the value of 112,000 obtained by viscosity measurements for the composite sample.

The polydispersity of each fraction was calculated from the weight-average and number-average molecular weights. It is interesting to note that the polydispersity of fraction 4 (Table 10) is greater than that of the composite sample. This is because both the weight-average and number-average molecular weights of fraction 4 are low and their ratio is high. The relative width of the distribution based on the difference between weight-average and number-average molecular weights is greater for the composite sample than for any of the fractions.

Molecular weight distribution curves were constructed to show the positions of the number-average and weight-average molecular weights. The peaks of both curves are higher than the calculated number-average and weight-average molecular weights for the composite sample. However, the areas on each side of the designated average molecular weight are approximately equal as would be expected. No attempt was made to extend the distribution curves to lower and higher molecular weight ranges because experimental points were not available. There is some evidence from the curves that the membrane was permeated by the low molecular weight fraction. This would give a lower osmotic pressure and a higher number-average molecular weight. If such permeation did not occur a lower number-average molecular weight would be obtained and the distribution function would decrease in value to produce a more uniform curve which could be extended towards the origin. For both the number-average and weight-average molecular weights the distribution curves are asymmetric about the designated average.

It is interesting to note that the slopes of the osmotic pressure plots are higher for Esso 373 grade PVC and its fractions than those obtained for the Esso 353 grade PVC. This indicates the likelihood that both grades were produced under different reaction conditions,since this would affect the shape of the molecules and the chemical properties.

CONCLUSIONS

A modified Fuoss-Mead block osmometer was found to be relatively simple to construct and use for routine osmotic pressure measurements. The use of micro-regulating valves to adjust meniscus levels made the instrument especially useful for dynamic measurements. The quick assembly of the instrument, simple filling procedure by means of a syringe and matching solution and solvent chambers were also desirable features. The all metal construction made it durable for repeated use.

A modified Bruss and Stross dynamic method in which meniscus levels were read during fixed time intervals was found to be the best of several methods for the rapid determination of osmotic pressure. This method was made possible by the level adjustment feature enabling flow rates to be measured for relatively few values of hydraulic head. The equilibrium osmotic pressure head at zero flow rate was determined by applying a least mean squares fit to the rate data.

By fractionating a commercial PVC sample and constructing a molecular weight distribution curve it was shown that by osmometry and viscometry, polymers could be well characterized as to their average molecular weight and degree of polydispersity. The combination of a simple osmometer and a reliable dynamic method which does not require additional calibration appears to be competitive with other methods of polymer characterization.

NOMENCLATURE

a - capillary cross-sectional area, cm.^{2}

A - membrane area, cm.^{2}

B - slope constant in the modified van't Hoff expression, cm. l.^{2}/g.^{2}

c - solution concentration, g./l.

d_1 - solvent density, g./cm.^{3}

g - acceleration due to gravity, 980 cm./sec.^{2}

h - hydraulic head difference between the two capillaries, cm. of solvent head.

h_o, h_1, h_2, h_3 - values of h at various time intervals, cm. of solvent head.

H - hydraulic head equivalent to osmotic pressure, cm. of solvent head.

k' - Huggins' slope constant.

k_p - membrane permeation constant, cm./min. cm. of solvent head.

K - Staudinger constant relating molecular weight to intrinsic viscosity.

L - membrane thickness, cm.

m - index constant in the equation defining Z-average molecular weight.

M - molecular weight, g./g. mole.

M_i - molecular weight of fraction i, g./g. mole.

$\bar{M}_n$ - number-average molecular weight, g./g. mole.

$\bar{M}_v$ - viscosity-average molecular weight, g./g. mole.

$\bar{M}_w$ - weight-average molecular weight, g./g. mole

$\bar{M}_z$ - Z-average molecular weight, g./g. mole

n - number of pores in a membrane.

n_i - number of gram moles of fraction i.

P - pressure differential causing flow through a membrane, dynes/cm.^{2}

Q - rate of flow through a membrane pore, cm.^{3}/sec.

R - gas constant, 82.06 cm.^{3} atm./g. mole ^oK.

R_a - radius of a membrane pore, cm.

t - time, min., sec.

T - temperature, ^oK.

w_i - weight of fraction i, g.

α - Mark-Houwink constant relating molecular weight to intrinsic viscosity.

ε - membrane porosity, pore volume/total volume of membrane.

η - solution viscosity, cp.

η_o - pure solvent viscosity, cp.

η_{sp} - specific viscosity, $\eta - \eta_o / \eta_o$.

$[\eta]$ - intrinsic viscosity, reduced specific viscosity at infinite dilution, l./g.

θ - function used to describe the weight distribution of molecular weights, g.

Π - osmotic pressures, dynes/cm.^{2}

ϕ - function used to describe the molar distribution of molecular weights, g. moles x 10^3.

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APPENDICES

A. VOLUME CALIBRATION OF OSMOMETER

To facilitate filling the osmometer with the correct amount of solution each time, the capacity of each chamber of the osmometer was measured using a small syringe. The volume of each chamber was found to be 1.8 ml. including the filling tube.

The variation of the meniscus levels with temperature for 0.5 mm. capillaries with THF was as follows:

TEMPERATURE (°C)	CAPILLARY LEVELS (cm.)
25.00	40.155
25.20	40.440
25.80	41.300

The calculated sensitivity based on the above results is 1.43 cm/C° and can be assumed constant over a small temperature range. If temperature is controlled to ± 0.01°C the levels can be read to ± 0.014 cm.

B. PERMEATION CONSTANTS

RUN NO. - M-1
MEMBRANE - S &S 08
SOLVENT - THF

DIRECTION OF FLOW	TIME (min.)	h (cm.)	h_o/h_t	k_p (cm./(min.)(cm. of solvent head))
A → B	0.0	2.790		
	5.0	2.230	1.25112	0.0448
	10.0	1.758	1.58703	0.0463
	15.0	1.455	1.91753	0.0435
	20.0	1.145	2.43668	0.0446
	25.0	0.890	3.13483	0.0458
	30.0	0.663	4.20814	0.0479
	36.0	0.465	6.00000	0.0499
B → A	0.0	2.770		
	5.0	2.230	1.24439	0.0438
	10.0	1.775	1.56338	0.0448
	15.0	1.430	1.94056	0.0443
	53.0	0.220	12.61364	0.0478

RUN NO. - M-2
MEMBRANE - S & S 07
SOLVENT - THF

DIRECTION OF FLOW	TIME (min.)	h (cm.)	h_o/h_t	k_p (cm./(min.)(cm. of solvent head))
A → B	0.0	8.020		
	5.0	3.985	2.01129	0.1400
	10.0	1.740	4.60632	0.1529
	15.0	0.955	8.39267	0.1420
	20.0	0.495	16.19191	0.1393
	25.0	0.280	28.62500	0.1343
B → A	0.0	4.855		
	5.0	2.168	2.23939	0.1615
	10.0	1.132	4.28887	0.1460
	15.0	0.433	11.21247	0.1612
	20.0	0.185	26.24324	0.1635

RUN NO. - M-3
MEMBRANE - S & S 08
SOLVENT - cyclohexanone

DIRECTION OF FLOW	TIME (min.)	h (cm.)	h_o/h_t	$\bar{k}_p$ (cm./(min.)(cm. of solvent head))
	0.0	4.181		-
	16.0	4.047	1.03311	0.00215
	22.0	3.923	1.06576	0.00293
A → B	60.0	3.185	1.31272	0.00462
	70.0	3.050	1.37082	0.00453
	80.0	2.915	1.43431	0.00454

RUN NO. - M-4
MEMBRANE - S & S 08
SOLVENT - THF

DIRECTION OF FLOW	TIME (min.)	h (cm.)	h_o/h_t	k_p (cm./(min.)(cm. of solvent head))
A → B	0.0	6.110		
	5.0	5.105	1.19589	0.0358
	10.0	4.095	1.49084	0.0400
	15.0	3.600	1.69583	0.0354
	20.0	2.668	2.28823	0.0415
	25.0	2.075	2.94217	0.0433
	30.0	1.645	3.71125	0.0438
	35.0	1.230	4.96342	0.0460
	40.0	0.910	6.70879	0.0477
	300.0	-0.350		
B → A	0.0	10.640		
	5.0	8.470	1.25502	0.0456
	10.0	6.917	1.53649	0.0430
	15.0	5.670	1.87478	0.0420
	20.0	4.670	2.27623	0.0412
	25.0	3.860	2.75389	0.0406
	30.0	3.202	3.31980	0.0400
	35.0	2.764	3.84587	0.0386
	40.0	2.347	4.52919	0.0379
	300.0	0.350		

Side B has an asymmetry pressure of 0.35 cm.

BRUSS AND STROSS METHOD FOR CALCULATING PERMEATION CONSTANTS

RUN	RATE (cm./min.)	h (cm.)	
M-1	-0.1100	2.510	
	-0.0940	2.000	
	-0.0330	0.562	
	0.1080	-2.500	Slope = -22.5
	0.0912	-2.002	
	0.0690	-1.602	
	0.0318	-0.825	
M-4	-0.1427	3.370	
	-0.0844	1.860	Slope = -25.4
	-0.0735	1.275	Intercept = -0.373
	0.1620	-4.260	
	0.0855	-2.770	

C. ANALYSIS OF ESSO 353 PVC BY OSMOMETRY USING VARIOUS METHODS

RUN NO. - 353-1

CONC. - 0.344 g./l. THF

TIME (min.)	SOLUTION LEVEL (cm.)	SOLVENT LEVEL (cm.)	h (cm.)
0.0	42.235	46.010	-3.775
5.0	42.625	45.680	-3.055
10.0	42.845	45.285	-2.440
15.0	43.010	44.960	-1.950
20.0	43.155	44.715	-1.560
30.0	43.415	44.420	-1.005
40.0	43.585	44.185	-0.600
50.0	43.760	44.065	-0.305
60.0	43.865	44.960	-0.095
0.0	44.260	39.745	4.515
5.0	43.862	40.180	3.682
10.0	43.536	40.490	3.046
15.0	43.280	40.750	2.530
20.0	43.115	40.950	2.165
30.0	42.800	41.236	1.564
40.0	42.615	41.445	1.170
50.0	42.510	41.625	0.885
60.0	42.450	41.745	0.705
300.0	42.100	41.790	0.310
720.0	42.030	41.725	0.305

ANALYSIS OF RUN 353-1

(a) Static reading = 0.305 cm.

(b) Fuoss-Mead half sum = 0.305 cm. at 60 minutes.

(c) Bruss and Stross method based on dynamic response curves:

RATE (cm./min.)	h (cm.)
0.1440	-3.415
0.1230	-2.747
0.0980	-2.195
0.0780	-1.755
0.0495	-1.253
0.0405	-0.803
0.0295	-0.453
0.0210	-0.200
-0.1660	4.098
-0.1270	3.364
-0.1010	2.780
-0.0730	2.348
-0.0600	1.864
-0.0390	1.367
-0.0285	1.028
-0.0180	0.795

H = 0.301 cm. based on a least squares fit. (See Figure 8).

Slope = -25.0 = $-1/k_p$

k_p = 0.040 (cm./(min.)(cm. of solvent head))

(d) METHOD OF PHILIPP

Points were taken at equally spaced time intervals from the dynamic curves and H was calculated from equation (12).

h1 (cm.)	h2 (cm.)	h3 (cm.)	H (cm.)
3.046	2.165	1.565	0.274
2.165	1.565	1.170	0.420
1.865	1.367	1.027	0.298
1.565	1.170	0.885	0.139
1.367	1.027	0.795	0.289
1.170	0.885	0.705	0.396
-1.950	-1.282	-0.802	0.426
-1.560	-1.005	-0.600	0.493
-1.282	-0.802	-0.452	0.489
-1.005	-0.600	-0.305	0.486
-0.802	-0.452	-0.200	0.454

Note: Many of the points were obtained by linear interpolation from the dynamic response curves.

(e) METHOD OF ELIAS

h (cm.)	RATE (cm./min.)	H (cm.)
-2.747	0.123	0.327
-2.195	0.098	0.255
-1.755	0.078	0.195
-1.282	0.055	0.105
-0.802	0.040	0.209
-0.452	0.029	0.285
-0.200	0.021	0.325
3.365	-0.127	0.184
2.790	-0.103	0.208
2.347	-0.073	0.522
1.865	-0.060	0.362
1.027	-0.028	0.315
0.795	-0.018	0.345
0.592	-0.009	0.365

The following runs were analysed in the same manner as Run 353-1. Only the results are summarized in table 6.

RUN NO. - 353-2 CONC. - 0.484 g./l. THF

TIME (min.)	SOLUTION LEVEL (cm.)	SOLVENT LEVEL (cm.)	h (cm.)
0.0	40.000	43.630	-3.630
5.0	40.290	43.190	-2.900
10.0	40.550	42.875	-2.325
17.0	40.786	42.450	-1.664
20.0	40.890	42.345	-1.445
30.0	41.183	41.990	-0.807
40.0	41.265	41.665	-0.400
50.0	41.350	41.470	-0.120
60.0	41.410	41.360	-0.050
0.0	43.230	38.910	4.320
5.0	42.795	39.305	3.490
10.0	42.555	39.570	2.985
17.0	42.215	39.835	2.380
20.0	42.125	39.965	2.160
30.0	41.772	40.200	1.572
40.0	41.585	40.345	1.240
50.0	41.435	40.500	0.935
60.0	41.405	40.595	0.810
300.0	38.444	37.992	0.452

RUN NO. - 353-3

CONC. - 1.250 g./l. THF

TIME (min.)	SOLUTION LEVEL (cm.)	SOLVENT LEVEL (cm.)	h (cm.)
0.0	42.295	44.515	-2.220
5.0	42.470	44.205	-1.735
10.0	42.640	43.845	-1.205
20.0	42.835	43.340	-0.505
30.0	42.970	43.035	-0.065
60.0	43.150	42.500	0.650
0.0	42.850	38.965	3.885
5.0	42.425	39.105	3.320
10.0	42.190	39.310	2.880
20.0	41.950	39.565	2.385
30.0	41.810	39.800	2.010
60.0	41.500	40.080	1.420
300.0	41.260	40.090	1.170

RUN NO. - 353-4

CONC. - 2.126 g./l. THF

TIME (min.)	SOLUTION LEVEL (cm.)	SOLVENT LEVEL (cm.)	h (cm.)
0.0	43.100	46.130	-3.030
6.0	43.500	45.420	-1.920
10.0	43.690	45.165	-1.475
15.0	43.885	44.735	-0.850
20.0	44.010	44.420	-0.410
30.0	44.195	43.960	+0.235
40.0	44.410	43.630	0.780
60.0	44.720	43.320	1.400
0.0	44.230	37.535	6.695
6.0	43.580	38.010	5.570
10.0	43.350	38.270	5.080
15.0	43.030	38.530	4.500
20.0	42.820	38.750	4.070
30.0	42.430	39.000	3.430
40.0	42.160	39.195	2.965
60.0	41.970	39.420	2.550
300.0	41.197	39.178	2.019

RUN NO. - 353-5 CONC. - 3.464 g./l. THF

TIME (min.)	SOLUTION LEVEL (cm.)	SOLVENT LEVEL (cm.)	h (cm.)
0.0	44.470	42.735	1.735
5.0	44.570	42.550	2.020
10.0	44.785	42.490	2.295
15.0	44.855	42.370	2.485
20.0	44.960	42.285	2.675
30.0	45.030	42.135	2.895
60.0	45.230	41.910	3.320
0.0	45.090	39.450	5.640
5.0	44.890	39.625	5.265
10.0	44.815	39.850	4.965
20.0	44.630	40.127	4.503
30.0	44.567	40.300	4.267
60.0	44.355	40.535	3.820
300.0	43.970	40.400	3.573

(f) MODIFIED BRUSS AND STROSS METHOD

The following solutions were analysed by pre-setting the levels and measuring the rate of change as a function of h for each separate point. Each point required only 5 minutes and results were fitted by the least mean squares method.

RUN NO. - 353-6 CONC. - 1.283 g./l. THF

TIME (min.)	SOLUTION LEVEL (cm.)	SOLVENT LEVEL (cm.)	h (cm.)	$h_{AV.}$ (cm.)	RATE (cm./min.)
0.0	42.840	46.105	-3.265	-2.905	0.144
5.0	42.230	45.775	-2.545		
0.0	43.255	43.255	0.000	0.085	0.034
5.0	43.350	43.080	0.170		
0.0	44.708	41.845	2.863	2.720	-0.0558
5.0	44.500	41.916	2.584		
0.0	43.995	41.925	2.070	2.022	-0.019
5.0	43.880	41.905	1.975		

H = 1.195 cm.

RUN NO. - 353-7 CONC. - 3.464 g./1. THF

TIME (min.)	SOLUTION LEVEL (cm.)	SOLVENT LEVEL (cm.)	h (cm.)	$h_{AV.}$ (cm.)	RATE (cm./min.)
0.0	47.105	40.960	6.145	5.915	-0.092
5.0	46.915	41.230	5.685		
0.0	46.945	43.575	3.370	3.378	0.003
5.0	46.970	43.585	3.385		
0.0	44.240	43.355	0.885	1.117	0.093
5.0	44.465	43.115	1.350		
0.0	44.660	42.035	2.625	2.702	0.031
5.0	44.740	41.960	2.780		

H = 3.570 cm.

D. ANALYSIS OF ESSO 363 PVC USING AN ASYMMETRIC MEMBRANE

Asymmetry pressure = 0.21 cm. on solution side.

RUN NO. - 363-1 CONC. - 1.554 g./l. THF

TIME (min.)	SOLUTION LEVEL (cm.)	SOLVENT LEVEL (cm.)	h (cm.)
0.0	42.345	42.345	0.000
5.0	42.745	42.205	0.270
10.0	42.600	42.105	0.495
20.0	42.790	41.980	0.810
30.0	42.900	41.900	1.000
40.0	42.987	41.880	1.107
50.0	43.028	41.866	1.162
60.0	43.080	41.887	1.193
145.0	43.330	42.115	1.215

H = 1.261 cm. by the conventional Bruss and Stross method.

METHOD OF PHILIPP

h_1 (cm.)	h_2 (cm.)	h_3 (cm.)	H (cm.)
0.270	0.652	0.905	1.395
0.495	0.810	1.000	1.288
0.652	0.905	1.053	1.265
1.000	1.107	1.162	1.220

RUN NO. - 363-2 CONC. - 2.333 g./l. THF

TIME (min.)	SOLUTION LEVEL (cm.)	SOLVENT LEVEL (cm.)	h (cm.)
0.0	40.820	40.250	0.570
5.5	40.880	40.093	0.787
10.0	40.955	40.000	0.955
20.0	41.050	39.845	1.205
30.0	41.145	39.755	1.390
40.0	41.195	39.700	1.495
51.0	41.250	39.645	1.605
63.0	41.295	39.640	1.655
71.0	41.315	39.640	1.675

H = 1.752 cm. by the conventional Bruss and Stross Method.

METHOD OF PHILIPP

h_1 (cm.)	h_2 (cm.)	h_3 (cm.)	H (cm.)
0.787	1.092	1.307	1.809
0.967	1.214	1.390	1.893
1.092	1.306	1.445	1.719
1.214	1.390	1.500	1.644

E. SOLUTION VISCOSITY MEASUREMENTS

Viscometer constant = 0.00416 cs./sec.

Solvent density = 0.885 g./cm.^{3}

Solvent viscosity = 0.469 cp.

Sample - Esso 353 PVC

CONC. (g./l.)	FLOW TIME (sec.)	η (cp.)	η_{sp}	$\eta_{sp/c}$ (l./g.)
0.344	130.2	0.480	0.0228	0.0663
0.484	131.5	0.484	0.0330	0.0682
1.114	137.3	0.506	0.0786	0.0689
1.250	138.3	0.509	0.0865	0.0692
1.670	142.2	0.523	0.1170	0.0701
2.126	146.2	0.538	0.1484	0.0698
3.464	159.0	0.585	0.2490	0.0719

Sample - Esso 363 PVC

CONC. (g./l.)	FLOW TIME (sec.)	η (cp.)	η_{sp}	$\eta_{sp/c}$ (l./g.)
0.958	138.0	0.508	0.0815	0.0851
1.278	141.6	0.521	0.1098	0.0859
1.917	148.9	0.548	0.1668	0.0870
3.834	172.7	0.635	0.3540	0.0925

Sample - Esso 373 PVC

CONC. (g./l.)	FLOW TIME (sec.)	η (cp.)	η_{sp}	$\eta_{sp/c}$ (l./g.)
1.175	145.8	0.536	0.1453	0.1237
1.765	155.6	0.572	0.2223	0.1259
2.350	166.8	0.613	0.3103	0.1320
3.526	188.3	0.693	0.4792	0.1359

F. ANALYSIS OF FRACTIONS OF 373 PVC

Each fraction including the composite 373 sample was analysed by the modified Bruss and Stross method.

ESSO 373 COMPOSITE SAMPLE:

CONC. (g./l.)	TIME (min.)	h (cm.)	$h_{AV.}$ (cm.)	RATE (cm./min.)
1.316	0.0	-0.185	0.035	0.0142
	31.0	0.254		
	0.0	0.426	0.460	0.0045
	15.0	0.494		
	0.0	0.254	0.340	0.0059
	29.0	0.426		
	0.0	0.494	0.540	0.0009
	92.0	0.585		

H = 0.593 cm.

CONC. (g./l.)	TIME (min.)	h (cm.)	$h_{\text{AV.}}$ (cm.)	RATE (cm./min.)
1.765	0.0	1.245	1.132	-0.0233
	10.5	1.010		
	0.0	-0.085	0.0475	0.0265
	10.0	0.180		
	0.0	0.535	0.595	0.0120
	10.0	0.655		
	0.0	1.905	1.780	-0.0250
	10.0	1.655		

H = 0.859 cm.

CONC. (g./l.)	TIME (min.)	h (cm.)	$h_{\text{AV.}}$ (cm.)	RATE (cm./min.)
1.975	0.0	-0.750	-0.575	0.0750
	5.0	-0.400		
	0.0	0.740	0.758	0.0070
	5.0	0.775		
	0.0	0.185	0.307	0.0245
	10.0	0.430		
	0.0	1.258	1.229	-0.0039
	15.0	1.200		

H = 1.042 cm.

CONC. (g./l.)	TIME (min.)	h (cm.)	$h_{AV.}$ (cm.)	RATE (cm./min.)
2.350	0.0	-0.015	0.105	0.0240
	10.0	0.225		
	0.0	0.585	0.655	0.0140
	11.0	0.725		
	0.0	1.100	1.136	0.0060
	12.0	1.172		
	0.0	1.700	1.512	-0.0043
	90.0	1.325		

H = 1.350 cm.

3.590	0.0	0.482	0.816	0.0636
	10.5	1.150		
	0.0	1.608	1.737	0.0257
	10.0	1.865		
	0.0	4.085	3.862	-0.0445
	10.0	3.640		

H = 2.563 cm.

FRACTION 1:

CONC. (g./l.)	TIME (min.)	h (cm.)	$h_{AV.}$ (cm.)	RATE (cm./min.)
0.555	0.0	0.145		
	300.0	0.143		
		H = 0.143 cm.		
	0.0	-0.590	-0.450	0.0280
	10.0	-0.310		
	0.0	0.080	0.100	0.0040
	10.0	0.120		
0.739	0.0	1.240	1.060	-0.0360
	10.0	0.880		
	0.0	0.705	0.605	0.0200
	10.0	0.505		
	0.0	0.335	0.302	-0.0065
	10.0	0.270		
		H = 0.182 cm.		

CONC. (g./l.)	TIME (min.)	h (cm.)	$h_{AV.}$ (cm.)	RATE (cm./min.)
1.110	0.0	0.560	0.520	-0.0080
	10.0	0.480		
	0.0	1.300	1.130	-0.0350
	10.0	0.950		
	0.0	-0.855	-0.638	0.0435
	10.0	-0.420		
	0.0	0.430	0.400	-0.0060
	10.0	0.370		
	0.0	-0.028	0.042	0.0140
	10.0	0.112		

H = 0.329 cm.

Note that the osmotic pressures of dilute solutions were measured by taking equilibrium (5 hour) readings. These pressures were too low to be determined accurately by dynamic methods.

All the other fractions were analysed in a similar manner. A summary of all the readings is given below.

SAMPLE	CONC. (g./1.)	H (cm.)	H/c (cm. 1./g.)	INTERCEPT (cm. 1./g.)	SLOPE (cm. $1^2/g^2$)
373 COMPOSITE	1.316	0.593	0.450	0.3574	0.0806
	1.765	0.859	0.487		
	1.975	1.042	0.527		
	2.350	1.350	0.574		
	3.950	2.563	0.665		
FRACTION 1	0.555	0.143	0.260	0.2072	0.0749
	0.739	0.182	0.246		
	1.110	0.329	0.296		
FRACTION 2	0.884	0.243	0.288	0.2570	0.0639
	1.125	0.391	0.348		
	1.688	0.629	0.373		
	3.376	1.572	0.467		
FRACTION 3	2.176	0.970	0.446	0.3092	0.0636
	4.352	2.537	0.582		
FRACTION 4	1.288	0.729	0.566	0.4550	0.0821
	1.931	1.171	0.607		
	3.863	2.987	0.774		
FRACTION 5	0.575	0.565	0.983	0.9370	0.0829
	0.767	0.763	0.995		
	1.150	1.199	1.041		
	2.300	2.594	1.125		

INTRINSIC VISCOSITIES OF THE VARIOUS FRACTIONS

SOLVENT FLOW TIME = 127.6 sec.

FRACTION NO.	CONC. (g./l.)	FLOW TIME (sec.)	η_{sp}	η_{sp}/c (l./g.)
1	0.555	138.2	0.0831	0.1497
	0.739	142.1	0.1136	0.1540
	1.110	149.5	0.1715	0.1545
2	0.844	143.4	0.1240	0.1470
	1.125	149.4	0.1712	0.1520
	1.688	160.6	0.2590	0.1535
	3.376	200.0	0.5680	0.1685
3	1.221	150.0	0.1755	0.1440
	1.630	157.3	0.2331	0.1433
	2.442	174.0	0.3640	0.1500
	4.883	232.0	0.8205	0.1680
4	1.850	154.0	0.2068	0.1117
	2.466	164.2	0.2868	0.1163
	3.700	184.6	0.4467	0.1207
5	0.575	131.7	0.0321	0.0558
	0.767	133.0	0.0423	0.0552
	1.150	136.0	0.0658	0.0573
	2.300	144.6	0.1330	0.0580

FRACTION NO.	$[\eta]$ (l./g.)	SLOPE ($l.^2/g.^2$)	HUGGINS' CONSTANT
1	0.1466	0.00760	0.353
2	0.1410	0.00807	0.403
3	0.1335	0.00700	0.393
4	0.1058	0.00390	0.348
5	0.0548	0.00146	0.486

G. CALCULATIONS

(a) Number-average molecular weight:

$$\left(\frac{\pi}{c}\right)_{c \rightarrow o} = \frac{RT}{M}$$

$$R = 82.06 \ \frac{\text{atm. cm.}^3}{\text{g. mole } ^{o}\text{K}}$$

$$T = 298.0 \ ^{o}\text{K}$$

$$\pi = \frac{g \ d_i \ H}{A} = \text{dynes/cm.}^2$$

$$c = \text{g./l.}$$

Sample calculation for 353 PVC by the static method (Table 2):

$$\left(\frac{\pi}{c}\right)_o = \frac{(0.898)(980)(0.885)}{(1.013)(1000)} = 0.768 \ \frac{\text{dynes cm.}^3}{\text{cm.}^2 \text{ g.}}$$

$$\bar{M}_n = \frac{RT}{(\pi/c)_o} = \frac{(82.06)(298.0)}{0.768} = 31{,}800 \text{ g./g. mole}$$

(b) $\bar{M}_n$ from equation (1) $= \dfrac{\sum n_i M_i}{\sum n_i} = \dfrac{\sum w_i}{\sum w_i/M_i}$

For 373 PVC based on fractions:

$$\bar{M}_n = \frac{4.6511}{\frac{0.2978}{137{,}500} + \frac{0.3825}{110{,}800} + \frac{2.4265}{92{,}300} + \frac{1.2754}{62{,}600} + \frac{0.2689}{30{,}400}} = \frac{4.6511}{0.06118} = 76{,}100 \text{ g./g.mole}$$

$$\overline{M}_w \text{ from equation (2)} = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum w_i \overline{M}w_i}{\sum w_i}$$

$$= \frac{43.40 + 52.00 + 310.00 + 121.00 + 10.80}{4.6511}$$

$$= 115{,}000 \text{ g./g. mole.}$$

All other calculations were of a routine nature and were carried out by substituting data into equations presented in the theory.