

## Optimum Method for Osmotic Pressure Measurements with Membrane-Permeating Solutes

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### Synopsis

Osmotic pressure experiments were conducted with PVC samples of different molecular weights dissolved in THF, using both a block osmometer and a Hewlett-Packard automatic osmometer equipped alternately with Schleicher and Schuell 07 and 08 membranes to optimize the procedure for accurate osmotic pressure measurements. It was found that, provided a flow of solvent could be maintained through the membrane and into the solution, an osmotic pressure of good accuracy was obtained even though the membrane was nominally much too coarse for the polymer analyzed.

### Introduction

Characterization methods for polymeric materials are becoming increasingly important as different new polymers and methods of production appear. Manufacturers of polymers require quality control tests that ensure constancy and uniformity of product, while users likewise require tests to ensure that the polymer supplied from different sources is of equivalent quality.

Osmometers are essential devices for characterizing high molecular weight polymers. Some commercial osmometers such as the Hewlett-Packard, Hallikainen, and Melabs instruments have been highly automated to give readings of osmotic pressure within minutes of samples introduction. Often some doubt exists as to the absolute accuracy obtained, however. Of particular concern is the choice of membrane and its porosity with respect to the polymer solution to be analyzed. The amount of low molecular weight polymer that permeates through the membrane can, under certain circumstances, have a considerable effect on the measured osmotic pressure, especially if the volume of the solvent chamber is very small compared to the volume of the solution chamber, as in the Hewlett-Packard osmometer, for example. The extent of permeation and, in addition, the effects of actual membrane asymmetry appear difficult, if not impossible, to separate and assess when they occur.

Even though more time consuming, it is much more convenient to study membrane processes using a block osmometer, where the solvent and solu-

tion chambers can be independently charged, pressures in each chamber independently varied, and actual flow rates through the membrane determined. By utilizing a well-designed block osmometer, it is possible to measure the extent of membrane asymmetry, to show the effect of polymer permeation through the membrane, and to analyze the actual flow characteristics of the membrane itself. It is therefore possible to assess whether the membrane pore size is fine enough for the particular polymer sample, and hence whether the osmotic pressure is reliable. Further, as indicated in this work, a particular method of operation for a block osmometer utilizing even a relatively coarse membrane can give osmotic pressures comparable to those for the best available membranes. Therefore, a particular method of operation in which the solvent is caused to flow (at very low flow rate) through the membrane into the polymer solution during most of the osmotic pressure determination is recommended, especially when there is some uncertainty as to whether the membrane is sufficiently fine for the low molecular weight material in the polymer sample.

It has been well documented<sup>1-5</sup> that dynamic methods for determining osmotic pressure are more rapid and yield more accurate results than equilibrium methods. The commercial high-speed osmometers likewise are based on the principle of a rapid approach to the equilibrium osmotic pressure. In a publication from this laboratory,<sup>6</sup> a slight modification to a previously reported dynamic method was made. It was considered that when the hydraulic head difference between two chambers of the osmometer was not in balance with the osmotic pressure, Poiseuille (laminar) flow of solvent occurred through the membrane. The flow rate through the membrane was linearly related to the imposed net hydraulic head or pressure difference. An equivalent statement would be that a hydraulic head equivalent to the flow through the membrane was additive (with due regard to direction of flow) to the hydraulic head equivalent to the osmotic pressure:

$$\Delta h = \Delta h_{\text{flow}} + \Delta h_{\text{osmosis}} \quad (1)$$

In principle at least, then, if the membrane flow characteristics were well known, it should be possible to determine the osmotic pressure by measuring the flow rate corresponding to any single hydraulic head between the osmometer chambers. Such an approach is perhaps an oversimplification of the membrane process because of some apparently irreversible adsorption of polymeric material on one side of membranes which causes membrane asymmetry. In addition, should some polymer permeate the membrane, an observable hydraulic head difference at the equilibrium condition would not yield a meaningful osmotic pressure head. It would still appear necessary, therefore, to measure the hydraulic head difference and corresponding flow rates through the membrane through a range of values to permit the linear extrapolation to an equilibrium head corresponding to zero flow through the membrane. In addition, it still appears necessary to determine the asymmetric pressure of the membrane before and after each series of experiments.

## EXPERIMENTAL

### Block Osmometer

A block osmometer of a design described previously<sup>6</sup> was used in these measurements. The main features included two essentially identical S.S. cylindrical blocks machined with concentric semicircular-shaped grooves, separated by a Schleicher and Schuell 65-mm membrane and clamped together. The  $1/8$ -in stainless steel inlet lines and outlet lines contained, respectively, small shut-off valves and microvolume-regulating valves. Tru-bore capillaries 0.508 mm in diameter were joined to the microregulating valves by Kovar connectors.

The osmometer was immersed in a constant-temperature bath controlled at  $25^\circ \pm 0.02^\circ\text{C}$ . The membranes were conditioned from pure ethanol to THF solvent while installed in the osmometer. Each chamber could be readily flushed by means of a syringe containing the desired solvent or solution and connected to the stainless steel lines by means of septum stoppers.

The relative liquid levels of solvent and solution in the capillaries were measured by means of a cathetometer capable of being read to 0.01 mm. Measurements of some low flow rates through the membrane required the full precision of the cathetometer.

It is sometimes desired to express the solvent flow through the membrane on the basis of membrane area exposed to solvent. The total area of all the concentric grooves can be estimated by a simple formula if the groove width is  $2L$  and the radius to the center of each groove is  $r_i$ :

$$A_{\text{membrane}} = 4\pi L \sum_i r_i \quad (2)$$

### Procedure for Determining Membrane Asymmetry and Osmotic Pressure

The procedure for measuring the membrane asymmetric pressure involved first ensuring that residual polymer not firmly adsorbed to the membrane was flushed away. The membrane and each chamber of the osmometer were washed with solvent at least six times at about  $1/4$ -hr intervals. Usually, the membrane was exposed to fresh solvent overnight for asymmetry measurements the following morning. Membranes displaying large asymmetric pressures ( $>0.5$  cm) were replaced by fresh membranes.

A positive solvent head was ascribed to the position when the head in one particular capillary was higher than in the other, and correspondingly a positive flow was associated with it. A large negative head then corresponded to a negative flow by this convention. As a result of asymmetry, it was possible to obtain negative flows with positive heads, and vice versa. Repeated values of flow rate for head differences initially decreasing from about  $+4$  cm to zero and finally increasing to  $-4$  cm were measured. The flow rate and head differences were obtained by taking initial and final elevations in both capillaries over an appropriate time interval (such as 5 min). While seemingly a simple procedure, when measuring heads to

within 0.01 mm, even a very slight motion of the cathetometer or osmometer effectively changed the head reading so that a self-correcting procedure was found to give most consistent results. The initial and final hydraulic head differences, in cm, were taken as

$$\Delta h_i = h_{1i} - h_{2i} \quad \text{and} \quad \Delta h_f = h_{1f} - h_{2f}. \quad (3)$$

An arithmetic average head difference during the time interval is expressed by

$$\Delta h_{\text{avg}} = 1/2 (\Delta h_i + \Delta h_f). \quad (4)$$

The volumetric flow rate, in cc/min, through the membrane in time  $\theta$  is

$$F = \frac{1}{2} (\Delta h_i - \Delta h_f) \frac{A_{\text{capillary}}}{\theta}. \quad (5)$$

The flow rate for a basis of a unit area of exposed membrane is

$$M = \frac{1}{2\theta} (\Delta h_i - \Delta h_f) \frac{A_{\text{capillary}}}{A_{\text{membrane}}}. \quad (6)$$

If there was no adjustment to the volume-regulating valves, it was necessary that the hydraulic head change in one capillary should be in the opposite direction but equal in magnitude to that in the other capillary:

$$\Delta h_1 = h_{1i} - h_{1f} = h_{2f} - h_{2i} = -\Delta h_2. \quad (7)$$

If there was a repeated difference, some leakage was indicated.

The method of determining flow rate and corresponding average hydraulic head differences was used for both asymmetric pressure and osmotic pressure measurements.

The polymer solutions were prepared by charging about 0.5 g of previously dried polymer into a 100-ml volumetric flask partially filled with THF solvent. After solution was complete, this taking about 1 hr, the volume was made up to 100 ml. Aliquots of the solution were withdrawn and diluted to lower concentrations in 50-ml flasks. Relatively low polymer concentrations (less than 6 g/l.) were used in these experiments for several reasons. In the dilute region, the reduced osmotic pressure in all cases appeared to be a linear function of concentration. In the more concentrated region, the reduced osmotic pressure is better fitted by a particular nonlinear function of concentration, as discussed by Arnett and Gregg.<sup>7</sup> Corrections for density differences between polymer solution and solvent in the capillary tubes were obviated with the low concentrations. In addition, solution of polymer was relatively rapid and possibility for agglomeration of polymer molecules in solution reduced.

### Comparison of Methods for Osmotic Pressure

Measurements were performed with two characterized PVC samples obtained from Pressure Chemical Company, designated as PV-2 and PV-4 and supplied as laboratory standards. The number- and weight-average

TABLE I  
Number-Average Molecular Weights Using Different Membranes  
and Flow Directions

Membrane	Block osmometer			Automatic osmometer
	Solvent into Solution	Solution into Solvent	Infinite time (24 hr)	
	Pressure Chemical PV-4: $\bar{M}_n = 54,000$ , $\bar{M}_w = 132,000$			
SS 08	47,000	46,400	48,300	47,900
SS 07	47,900	51,500	59,200	50,800
	Pressure Chemical PV-2: $\bar{M}_n = 25,500$ , $\bar{M}_w = 68,600$			
SS 08	26,100	26,200	27,500	26,100
SS 07	27,300	31,600	39,300	28,300

molecular weights as indicated by the supplier are listed in Table I. The two samples, PV-2 and PV-4, were stated to have number-average molecular weights of 25,500 and 54,000, respectively. All osmotic pressure measurements were made with one of two types of Schleicher and Schuell membranes: (1) type 07 (coarse), designated for number-average molecular weights of over 80,000, and (2) type 08 (fine), designated for number-average molecular weights of over 20,000. The 07 membrane was purposefully chosen as an example of one much too coarse for the polymer samples to be analyzed.

Three types of osmotic pressure measurements were performed in succession for each polymer sample using the block osmometer. For the first type of measurement, flow rate-hydraulic head readings for decreasing heads were obtained corresponding to decreasing flows of solvent through the membrane into the solution. Subsequently, increasing flow rates and corresponding hydraulic heads were measured for increasing flows in the reverse direction through the membrane. In the first half of the experiment, the polymer solution would not be expected to permeate through the membrane because the flow of solvent was considered to prevent diffusion in the opposite direction. For the second portion of the experiment, some permeation would be expected because solvent (and possibly low molecular weight polymer) was being forced through the membrane, with the membrane acting essentially as a filter for the larger molecular weight polymer.

In the second experimental method performed immediately after the first, the flow rate-hydraulic head measurements were conducted exactly in the reverse direction to the first experiment. The initial flow rate from the solution to the solvent chamber was made relatively large and then decreased incrementally to zero; then finally, increasing solvent flows were directed through the membrane. It can be noted that if low molecular weight polymer permeated the membrane in any appreciable quantity during the second experiment, a different relation would be obtained between the hydraulic head and flow rate; the effective osmotic pressure would be expected to be reduced because of the presence in the solvent of the low

molecular weight polymer. Thus, the difference in the two hydraulic head-flow rate lines would represent some measure of permeability of the particular polymer through the membrane.

The third experiment, again performed in succession after the first two, consisted in simply waiting for a prolonged period of time (usually about 24 hr), during which equilibrium was considered to have been established, and obtaining a reading of hydraulic head equivalent to the prevailing osmotic pressure. It was considered that low molecular weight polymer would continue to permeate the membrane by molecular diffusion if the size of the membrane pores were larger than the diffusing molecules. The osmotic pressure so determined was expected to be much too low, particularly for the relatively coarse 07 membrane.

For accurate osmotic pressure measurements, it was found necessary to measure the extent of membrane asymmetry before and after each series of (three) experiments. It was found that in spite of repeated washings with solvent of the solution chamber, a small but gradually increasing asymmetric pressure was observed in a direction indicating a possible irreversible adsorption of polymeric material on the polymer solution side of the membrane. The change during a single series of experiments was usually small ( $<0.1$  cm), but quite significant when compared with the actual osmotic pressures measured. For the purpose of correcting hydraulic head readings for asymmetric pressure, any change in asymmetric pressure was assumed to have occurred during the prolonged equilibration period.

It is perhaps necessary to semiquantitatively describe the magnitude of the flow rates utilized in establishing the flow rate-hydraulic head relationship. The internal cross-sectional area of the precision-bore capillaries was approximately 0.002 sq cm. Displacements of interface level were usually of the order of 0.3 cm during a normal measuring time interval of from 3 to 5 min. Hence, for a complete series of about ten flow measurements, the total flow through the membrane in both directions was of the order of 0.006 cc. This volume can be compared with the volume of each chamber, excluding valves and tubing of about 0.70 cc. The concern in this case was that the concentration in each chamber did not appreciably change during the actual measurement. When a series of experiments was to be performed with a new polymer solution, the solvent chamber of the osmometer was flushed and filled with fresh solvent to ensure minimum contamination of the solvent with residual low molecular weight polymer.

#### **Hewlett-Packard Automatic Osmometer**

For comparison with block osmometer measurements, a Hewlett-Packard Model 501 automatic osmometer equipped with membranes of the same type as used with the block osmometer and preconditioned to THF solvent was utilized. The automatic osmometer, operated at 25°C, was used in conjunction with a recorder to aid in the determination of steady-state pressures.

A fourth set of osmotic pressure measurements was performed with each polymer solution using the Hewlett-Packard automatic osmometer. The principle of operation entailed a servomechanism designed to correct the elevation of a solution-leveling bottle to that position for which there was no flow through the membrane. It was observed that during measurement the leveling bottle moved up and down through cycles in which the movement gradually decreased in amplitude until it finally reached a steady position. During the cyclic motion, it is considered that some flow, albeit small, occurred through the membrane in both directions. In fact, the effect was expected to be not inconsequential because some solution was forced into the solvent chamber before any measurement was made. In addition, the volume of the solvent chamber was much smaller than the solution chamber, so that any permeation through the membrane could be expected to have a magnified effect. The effect of the small volume of the solvent chamber of the Hewlett-Packard (formerly Meckrolab) osmometer has been well discussed by Ghosh and Swenson.<sup>8</sup> The comparison of results with a high-speed commercial osmometer and a block osmometer was therefore of considerable interest.

Another characteristic of the automatic osmometer was that a membrane asymmetric pressure could not actually be measured by itself. It was possible for the solvent chamber to become contaminated with low molecular weight polymer, or the membrane to become asymmetric during continued use without any method for ascertaining which of, or to what extent, these events occurred. It should be noted, however, that the normal method of operation for this type of osmometer was self-correcting in that the hydraulic head (or position of leveling bottle) was obtained for a pure solvent in the sample chamber and then compared with that for a polymer solution. In this manner, the effects of contamination and possible asymmetry were properly accounted for. Although nowhere recommended, it would appear entirely possible to measure osmotic pressure by filling the solvent chamber with a *polymer solution* and then following the normal procedure.

### Waters Gel Permeation Chromatograph

A Waters Model 201 GPC was employed to indicate qualitatively the molecular weight distribution of the polymer samples. A solution concentration of about 0.1 wt-% was utilized, along with a THF solvent flow rate of 1 cc/min through two 4-ft columns in series in both the reference and sample circuits having gel pore sizes from  $5 \times 10^4$  to  $1.5 \times 10^5$  Å and from  $5 \times 10^3$  to  $1.5 \times 10^4$  Å. While an insufficient range of samples was available for actual calibration of the GPC for PVC polymer, it was possible to observe a distinct difference in elution times for samples of different polydispersity. A calibration for PVC using a GPC was alluded to by Pedersen,<sup>9</sup> but actual pertinent details for comparison were not included in his paper.

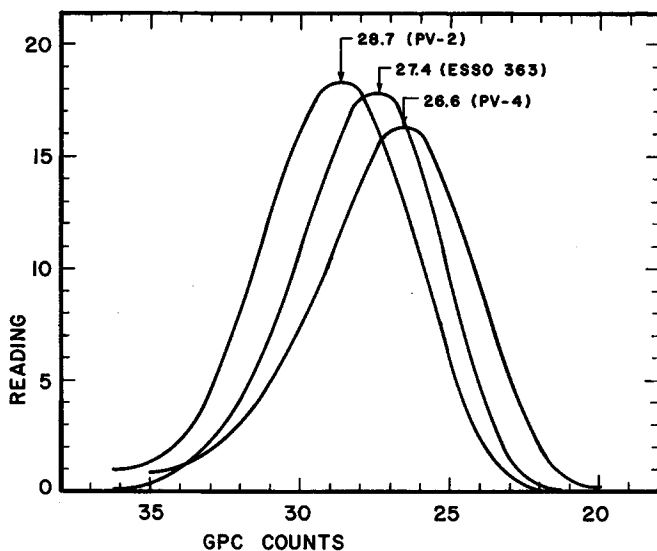


Fig. 1. GPC analyses for PV-2, PV-4, and Esso 363 polymers.

In a final series of measurements, the PVC samples PV-2, PV-4, and, in addition, a sample of commercial polymer Esso-grade 363, produced by Imperial Oil Enterprises using a suspension polymerization process, were analyzed by GPC. While the peak positions and widths of distribution could be compared to those corresponding to polystyrene, this appeared unnecessary for our experiments. It appeared desirable only to show that the molecular weights of PV-2 and PV-4 were significantly different and that the distributions were similar to that for a typical commercial product as shown in Figure 1.

## RESULTS AND DISCUSSION

The flow characteristics of the SS 07 and 08 membranes as well as the asymmetric pressures obtained with the block osmometer are shown in Figure 2. It is noted that the imposed pressure drop-versus-flow rate relation appears to be essentially linear. Such a linear relation would be expected if the membrane was not distorted in any way and for Poiseuille flow through it, particularly if the effective pore length through the membrane was considerably greater than the effective pore diameter. It can be observed from Figure 2 that the flow through the 07 membrane for the same pressure difference is about twice that through the 08 membrane. If it is considered that both membranes are of equal thickness (similar length of pores) and average percentage porosity or voidage, then the effective pore diameter would be also approximately twice as great in the 07 membrane.

The asymmetric pressure was obtained by one of two methods. The first involved fitting a least-squares line to the hydraulic head flow rate



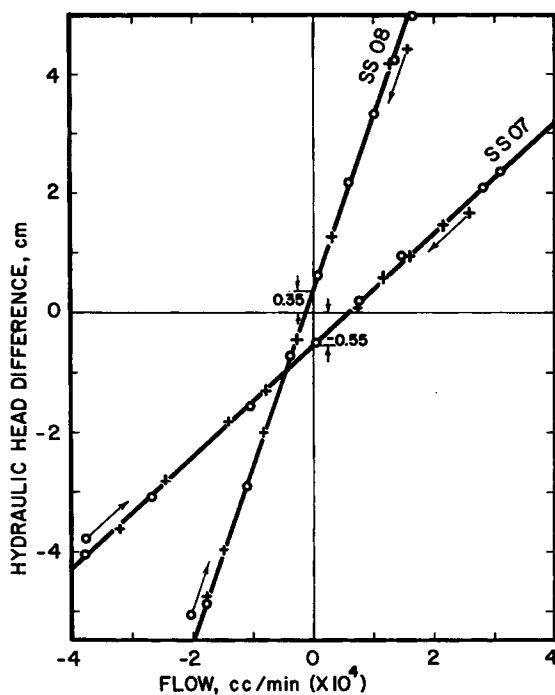


Fig. 2. Asymmetry pressures and flow characteristics for SS 07 and SS 08 membranes with THF solvent at 25°C.

data and obtaining a value for the hydraulic head corresponding to zero flow. The second involved simply waiting 8 to 12 hr to obtain what was considered to be an equilibrium asymmetric pressure reading. The asymmetric pressures obtained by the two methods usually agreed closely. It is noted that the flow characteristics of different membranes of the same type were often quite different, and hence the membranes could not be considered completely uniform. An interesting result was observed for the change in asymmetric pressure with both the 07 and 08 membranes as they were repeatedly used with different polymer solutions. The asymmetric pressure gradually increased in the direction suggesting increasing polymer adsorption on the side of the membrane exposed to the polymer solution. After continued use, asymmetric pressures of up to about 0.5 cm were observed. Repeated washings of the solution chamber and prolonged soaking with solvent only slightly reduced the asymmetric pressure. The supposed adsorption appeared essentially irreversible. The flow characteristics of the membrane did not appear to be affected by repeated use, however, suggesting that neither did adsorption occur to any significant extent within the pores, nor did the membrane continue to swell to significantly change the size or configuration of the pores.

In Figure 3 are shown the flow rate-hydraulic head measurements for the PV-2 sample with the 08 membrane from which osmotic pressures were

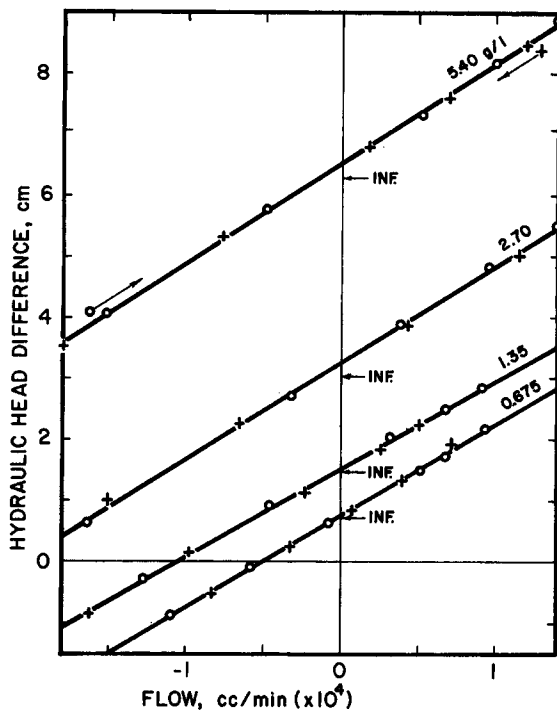


Fig. 3. Osmotic pressures for PV-2 solutions using SS 08 membrane. The symbol INF. is used to indicate the reading obtained after approximately 24 hr had elapsed.

obtained. The points obtained with the flow of solvent predominantly into the solution are differentiated from those in the reverse direction. Both sets of points for all concentrations appear to be coincident with the same linear relation. This would suggest that permeation of the membrane was minimal, even though the weight-average molecular weight of the sample was relatively low at 26,000. Further, the slopes of the lines in Figure 2 are similar suggesting that the same flow characteristics (essentially for pure solvent) are obtained for the fluid flowing through the membrane regardless of the polymer concentration. With this type of membrane and polymer sample, it is apparent that any method of measurement, even the equilibrium method, would give a relatively reliable result. A similar observation could be made for the result obtained for the PV-4 sample with the 08 membrane. The equilibrium method referred to here entails simply charging one chamber of the osmometer with solvent and the other with the polymer solution to approximately equal hydrostatic levels and waiting for osmotic equilibrium to become established.

The osmotic pressure measurements for the PV-2 sample using the (coarse) 07 membrane are shown in Figure 4. This membrane, specified to retain polymer molecules of molecular weight 80,000, was used in an attempt to measure an average polymer molecular weight of about 26,000. A large difference can be observed between those points obtained with flow

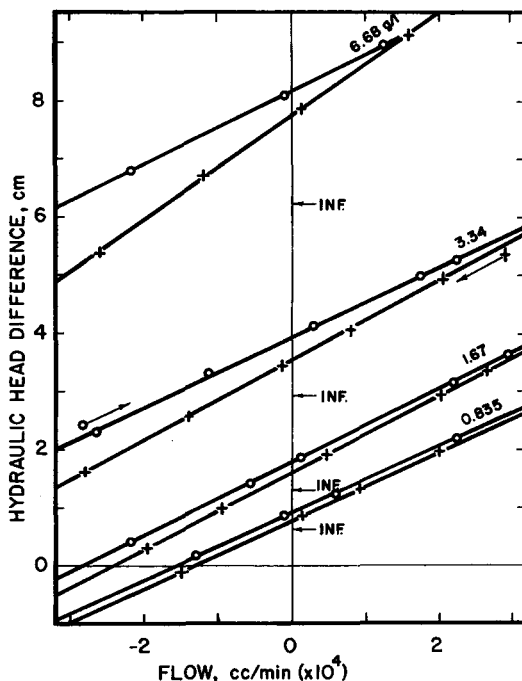


Fig. 4. Osmotic pressures for PV-2 solutions using SS 07 membrane.

of solvent predominantly into the solution when compared with the reverse flow. Such differences would yield gross errors in molecular weight determinations. The gross error for this series of measurements is confirmed in the combined results tabulated in Table I. Of particular interest, however, is that even with the grossly coarse membrane for the polymer concerned, the measurement made with solvent flowing through the membrane and into the polymer solution yields an osmotic pressure and average molecular weight (27,300) quite comparable to that obtained with the 08 membrane (26,100). If the experiment had been performed with flow in the reverse direction, the resulting average molecular weight would have been 31,600, or for an "equilibrium" osmotic pressure it would have been 39,300. The additional comparison in Table I is that the automatic osmometer equipped with an 07 membrane yielded a molecular weight higher (and presumably in greater error) than that obtained with the block osmometer using a flow of solvent into the solution.

It is evident from Table I that because of membrane permeation, the resulting average molecular weights are too high. If it is assumed that the differences indicated in Table I are mainly the result of permeation, then the most accurate osmotic pressure measurements would be those corresponding to experiments in which the solvent flowed through the membrane into the solution. It has been estimated that individual molecular weight measurements are accurate to within 4%. On this basis, the value

quoted by the Pressure Chemical Company for PV-4 would appear somewhat high, while for PV-2 the comparison is favorable. Table I can be interpreted as indicating that the automatic osmometer equipped with a membrane nominally too coarse for the particular sample would yield molecular weights that were too high, in spite of the rapidity in achieving equilibrium and minimum amount of flow through the membrane. Even with a fine (08) membrane, dynamic methods rather than an equilibrium method would appear to be essential for accurate results.

Rudin and Benschop-Hendrychova<sup>10</sup> reported for PV-2 and PV-4 samples dissolved in THF molecular weights at 27°C of 36,000 and 54,500, compared with 25,500 and 54,000 quoted for those particular lot samples by the Pressure Chemical Company. The measurements were reported to have been made with a Hewlett-Packard automatic osmometer equipped with a gel cellophane membrane of unspecified porosity. The polymer solution concentrations utilized were diluted from a 20 g/l. stock solution, about three times more concentrated than that used in this work. One aspect of the study concerned clustering or aggregation of PVC in THF solvent, which was considered to be most prevalent at a temperature of about 45°–60°C, at highest solution concentration, and for highest molecular weight polymer. Yet, the reported average molecular weight of PV-2 in THF at 45°C was 32,900, which was lower than at 27°C but much higher than that of the Pressure Chemical Company. In experiments performed in this laboratory at 25°C using relatively dilute THF solutions (less than 6 g/l.) some of which were stored for two or three days before measurement, no evidence of aggregate molecule formation was observed. One could question, therefore, whether in their experiments Rudin and Benschop-Hendrychova used a fine enough membrane, particularly for the low molecular weight PV-2 sample. One might also consider that aggregate molecule formation is highly concentration dependent so that while at low concentrations it does not occur to any significant extent, it does occur at somewhat higher concentrations.

The fact that a relatively coarse membrane could be used to measure osmotic pressures with reasonable accuracy is contrary to the postulates of Staverman and co-workers<sup>11</sup> who stated in essence that a deficiency of osmotic pressure has to be expected whenever the membrane is permeable to the solute. While it may be true that for a process which is in hydrodynamic and osmotic equilibrium the principles of Staverman and co-workers could be applied, it is apparent that as stated they cannot apply when there is an actual solvent flow through the membrane. There can be little question from these experiments that some of the sample is capable of permeating the membrane, but is simply prevented from doing so by a continuing small flow of solvent. In addition, it would appear that the molecules are indeed capable of causing an osmotic pressure even though they are smaller than the membrane passages. Indeed, the polymer solute may be actually separated from the membrane surface by a thin layer of pure solvent as it flows through the membrane.

In an attempt to simulate and greatly amplify what occurs in the automatic osmometer, a PV-2 sample was analyzed in the block osmometer

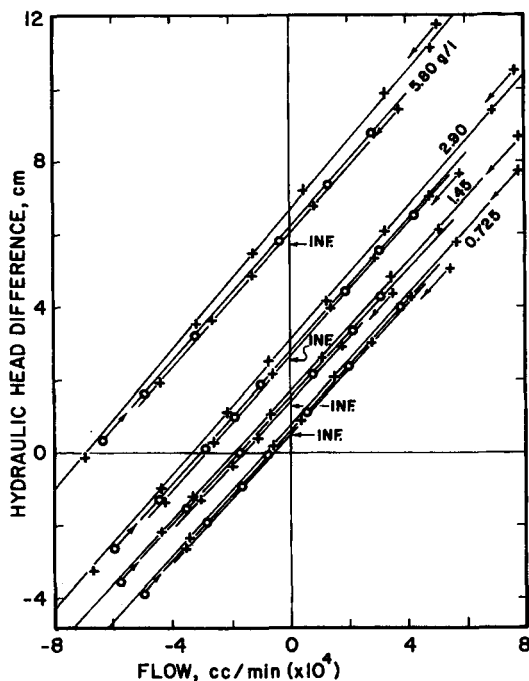


Fig. 5. Osmotic pressures using SS 07 membrane with reversing flows through membrane.

using an 07 membrane and a reversing-flow procedure. Hydraulic head-flow rate measurements were initially obtained for flows of solution into the solvent for incrementally reduced hydraulic heads, and subsequently for increasing flows in the reverse direction. This initial hydraulic head-flow rate relationship was used to determine the molecular weight corresponding to flow of solution into the solvent as listed in Table I. The procedure was repeated twice more with each solution, with the resulting flow rate-hydraulic head data as shown in Figure 5, which indicates that the effective osmotic pressure seemingly decreases with continued flow of solvent and solution through the membrane. In Figure 5 is also shown an osmotic pressure reading obtained after a 24-hr period, indicating an even greater permeation of polymer through the membrane. Such a procedure is clearly to be avoided for osmotic pressure measurements of permeating polymer solutions.

The linearity and slope of the lines in Figures 3-5 permit some speculation about the processes occurring on either side of the membrane during flow through it. In the very first stage of the experiment, a linear relation was obtained between the flow rate and hydraulic head for decreasing solvent flows. When the flow was reversed and polymer solution was forced through the membrane, it might have been expected that the membrane would be permeated by low molecular weight polymer, with a resulting decrease in effective osmotic pressure observable by a possible discontinuity in the head-flow line or at least a change in slope. Because neither of these were observed some explanations are required. It is postulated that low

molecular weight polymer does permeate the membrane contaminating the solvent, as verified by the subsequent decrease in effective osmotic pressure, but that, as the solvent is forced through the membrane, a filtration effect occurs causing a localized increase in polymer concentration at the membrane surface. Thus, the effective osmotic pressure would initially correspond to a concentration difference between solvent contaminated with low molecular weight polymer and that of a polymer concentration locally increased because of an accumulation of high molecular weight molecules at the membrane surface. The local increase in concentration on one side of the membrane would appear to be counterbalanced by the contamination on the other.

These experiments suggest a test by minor variation in method of operation of block osmometers to determine whether or not the membrane is appreciably permeated by polymer. Also presented is the method of operation to obtain the most accurate osmotic pressure with a given membrane. Unless such a test is performed or the method used, there is a danger of erroneously ascribing deviations from expected average molecular weights to some cause other than simply membrane permeation, with possible confusion in interpretation of data.

### Nomenclature

$A_{\text{capillary}}$	internal cross-sectional area of osmometer capillaries, $\text{cm}^2$
$A_{\text{membrane}}$	exposed membrane area, $\text{cm}^2$
$F$	flow rate through membrane, $\text{cc}/\text{min}$
$h_1, h_2$	elevations of liquid in capillaries 1 and 2, respectively, $\text{cm}$
$\Delta h$	difference in liquid elevations, $\text{cm}$
$M$	flow rate through membrane, $\text{cc}/\text{min}$ , per $\text{cm}^2$ exposed membrane
$\theta$	time interval, $\text{min}$

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