

Diffusion, Membrane Selectivity, and Nonequilibrium Effects in Rapid Membrane Osmometry

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Synopsis

Rapid membrane osmometry, narrow distribution polystyrenes in the range 4000-700,000, and three membrane types of different porosity were used to study the effects of diffusion and of Staverman membrane selection in osmometry. It was found that equilibrium was not obtained in the rapid measurement with the two densest membranes which led to grossly low values for the high molecular weight sample but had small effect at low molecular weights. Because of membrane selectivity effects at lower, and of nonequilibrium effects at higher molecular weights, the effective range was about 4000-350,000 for the densest membrane, 90,000-500,000 for the medium porosity membrane and from 145,000 to an unrestricted upper limit for the grossest membrane. A unique characteristic of the Mechrolab 501 instrument used in the study is the small constant volume on the solvent side of the membrane which allows determination of the osmotic pressure of the diffused material and its concentration when the molecular weight is known. Diffusion can be avoided if the pressure reading is taken quickly enough but membrane selectivity effects cannot be avoided if diffusible solute is present. Enormous selectivity effects were found when mixtures of diffusible and nondiffusible molecules were measured. Experimental values of the selectivity coefficient S_n of the mixtures were found to agree closely with those calculated from the Staverman equations. Estimates of the coil size of the polymers are given to provide an estimate of the effective porosities of the membranes.

INTRODUCTION

The problem of permeating solutes in osmotic pressure measurements has been considered theoretically by Laidler et al.¹⁻³ and Tung⁴ from kinetic considerations and by Staverman^{5,6} from nonequilibrium thermodynamic considerations. To overcome the error from diffusion, several dynamic methods have been proposed by many workers⁷⁻¹² to obtain theoretical or near-theoretical osmotic pressure by measuring the rate of permeation quickly and extrapolating to zero time. That the error in experimental osmotic pressure is not solely due to diffusion loss was shown by Staverman⁵ who predicted that the molecules small enough to permeate the membrane will not exert full osmotic pressure. This was well verified by Alvång and Samuelson¹³ by static osmometry.

The advent of rapid membrane osmometry and the availability of narrow distribution polystyrenes as well as uniform membranes now allow one to

study the effect of diffusion and reflection more easily and in greater detail than before.

The Mechrolab instrument used in this work (Mechrolab Inc. model 501 membrane osmometer)¹⁴ detects solvent flow by an optical system focused on an air bubble in a capillary on the solvent side of the membrane. This operates a servo system and the vertical movement of a solvent reservoir which adjusts the internal pressure on the solvent side as the bubble tries to move with the solvent in response to the change of pressure. There is thus no net flow of solvent or solute if the reading can be made quickly enough.

A unique characteristic of the instrument is the small, constant volume of the solvent side of the membrane. Upon replacing the solution with the solvent, the instrument allows one to measure the osmotic pressure of the diffused material. When the molecular weight of the material is known, the concentration of the diffused material can then be calculated.

Although the rapidity of the measurement is not expected to minimize the Staverman effect, the availability of narrow distribution polymers of known molecular weight allows one to mix diffusible with nondiffusible molecules in varying proportions to obtain the combined effects of diffusion and reflection as it might occur in polymers of broader distribution. Membranes of varying porosity are used in this study.

EXPERIMENTAL

Osmometer

The volume on the solution side of the osmometer obtained by liquid displacement between the scribe mark on the sample stack and the top of the exit stack was 0.48 ml. To determine the volume on the solvent side the width of the grooves on the plate were measured with a calibrated microscope and their depth with a fine caliper while their shape was assumed from microscopic inspection to be the arc of a circle. The volume of the plate hole was measured and the capillary volume from the top of the air bubble was obtained by mercury filling. The total volume on the solvent side was calculated to be 4.46×10^{-3} ml., about a hundredfold less than the volume of the solution side of the osmometer.

The temperature in the instrument was held at 25°C., slightly above that of the surrounding controlled room. Stock concentrations of 0.25–1.0% were used for the lowest and highest molecular weight, respectively, in order to maintain the pressure readings within measurable limits. Sorption of the solute to the membrane was allowed to occur routinely before measurements were made except where rapidly diffusing systems were measured.

Diffusion of the polymer through the different membranes was followed by recording the decrease in osmotic pressure.

Membranes

Descriptions of the membranes and the time required for equilibration with toluene on both sides of the membranes are given in Table I. Although recommended for use in water, the membranes had better selectivity than those recommended for organic solvents by the supplier, Schleicher and Schuell Co. Manufactured by Membran Gesellschaft, Göttingen, the membranes are apparently similar to those earlier described as fein, feinst, and aller feinst.

TABLE I
Pore Diameter and Solvent Equilibration Time of the Membranes

Membrane	Given pore diameter, A.	Time to equilibrate with toluene, min.
B-18	100-200	$1/4-1/2$
B-19	50-100	1-2
B-20	50	15-20

Occasional membranes were discarded when equilibration time and servo response with solvent alone were not typical of the average membrane type. High reproducibility with different solvents and different membranes of the same porosity has been reported by Linnell,¹⁵ who used Schleicher and Schuell 07 membranes to analyze glucomannan triacetate in 1,2-dichloroethane.

Diffusion

A polystyrene sample of $\bar{M}_n = 10,000$ [$\bar{M}_w/\bar{M}_n = 1.06$] and the grossest (B-18) membrane were used to illustrate diffusion effects.

A plot of $H - H_0/C$ versus concentration where the differences of H and H_0 are taken at each concentration at $t = 0$ and $t = 15$ min. is shown in Figure 1. H is the osmotic height of the solution and H_0 that for the solution. Diffusion of 75-85% would be required to explain the great drop of $(H - H_0)$ from $t = 0$ to that at $t = 15$ min. It is actually due to the drop of H_0 which is explained when it is recalled that the volume on the solvent side of the osmometer is only one hundredth of that of the solution side so that a diffusion of only 1% of the solute is sufficient to obtain a similar concentration on each side of the membrane.

Figures 2 and 3 illustrate the sequence of events which occur with a permeable membrane in the osmotic pressure determination.

S_0 and S in Figure 2 represent the solvent and the solution, respectively, in the osmometer, and the dotted line represents the membrane. At position A in both figures there is solvent on both sides of the membrane and no net flow occurs. Solvent is then replaced by solution and position B in the figures represents the immediate effect due to solute before diffusion has begun. Then diffusion starts and as more molecules enter the small volume on the solvent side (drawn of equal size in the sketch) the difference

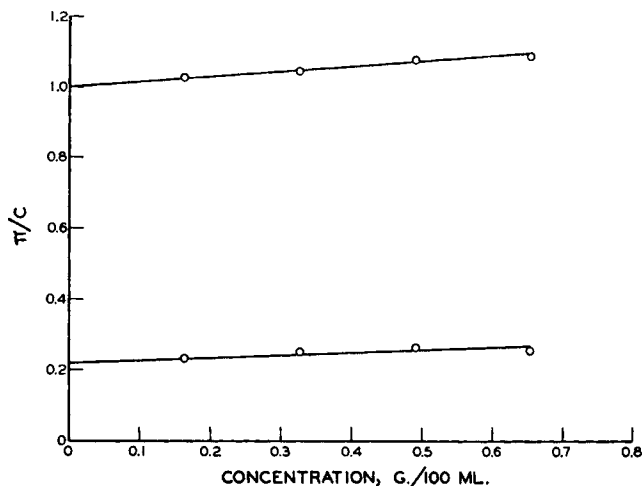


Fig. 1. Plots of $H - H_0/C$ vs. C for polystyrene of molecular weight 10,300 on membrane B-18 at $t = 0$ min. and $t = 15$ min. of diffusion.

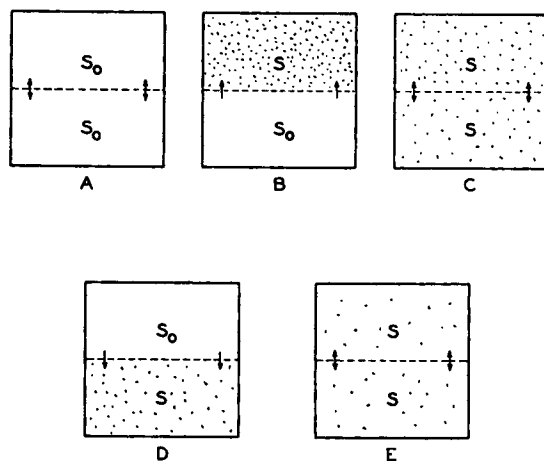


Fig. 2. Sequence of events in the osmometer during pressure measurements with permeating solutes; S = solution, S_0 = solvent; the broken line represents the membrane.

in chemical potential diminishes and at position C there is no net flow from either side as anticipated by Tung.⁴ At this point the solution is replaced by the solvent, and the upper cell now virtually becomes the solvent cell at position D, and H_0 drops to the extent dictated by the concentration in the lower side. As back diffusion now proceeds, position E approaches the level at position C where again no net flow will occur. Assuming that the difference AD (Fig. 3) represents the osmotic pressure of the diffused solute, its concentration can be calculated since the molecular weight of the sample and the volume of the solvent cell are known.

The real and apparent diffusion calculated on this basis are given in Table II. It is seen that the concentration on the solvent side calculated in this way is somewhat less than that of the original solution. Sorption

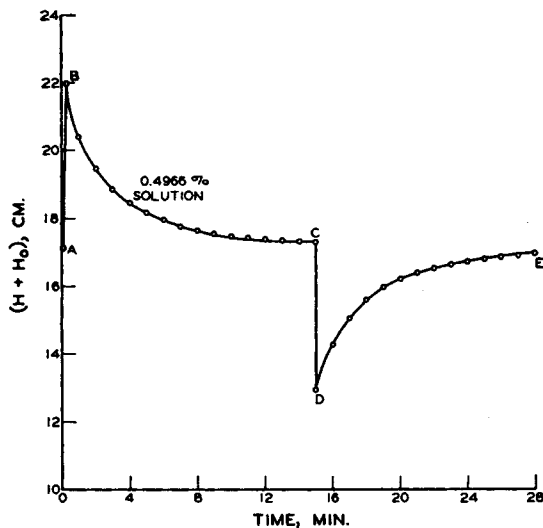


Fig. 3. Plot of $H + H_0$ vs. time of measurement with polystyrene of molecular weight 3670 on membrane B-18. A, B, C, D, E, represent the positions A, B, C, D, E in Figure 2.

to the membrane can be assumed to have lowered the total concentration since in this case prior sorption to the membrane could not be done easily before the actual measurements. Inaccuracy in noting the rapidly changing reading at position D is also present.

TABLE II
Real and Apparent Diffusion of Sample 11a Through Membrane B-18

Concn. of soln. at $t = 0$ in the soln. cell, g./l.	Initial Reading at $t = 0$, cm.	Final reading after solv. replaced soln., cm.	π of diffused solute, cm.	Concn. of diffused solute, g./l. ^a	Apparent diffusion, wt.-%	Real diffusion, wt.-% ^b
1.655	17.08	15.86	1.22	1.278	77.2	0.766
3.310	17.12	14.68	2.44	2.518	76.0	0.745
4.996	17.07	12.98	4.09	4.135	83.2	0.772
6.620	17.05	11.38	5.67	5.601	84.6	0.785

^a Calculated from the slope and intercept at $t = 0$ in Fig. 1.

^b Calculated from knowledge of cell volumes on either side of the membrane.

Staverman Effect with Single Solutes and with Mixtures of Diffusible and Nondiffusible Solutes

It has been shown that the effects of diffusion can be largely overcome in the rapid osmometer if one reads the pressure immediately as at position B in Figure 3. Rapid measurement however in no way minimizes the selectivity effect when diffusible solute is present. Staverman⁵ has derived the equation

$$\pi_{\text{ex}} = S \pi_{\text{th}} \quad (1)$$

where π_{ex} and π_{th} are the experimental and theoretical osmotic pressures and S is obtained from $(1 - S)$, which is the ratio of the solute in the membrane to that of the solution outside the membrane when the concentrations are identical on both sides of the membrane. It is thus a kind of partition coefficient which is a measure of the selectivity of the membrane.

In the case of mixed solutes, the number-average selection coefficient of the different components is defined by

$$S_n = \sum s_i n_i / \sum n_i \quad (2)$$

where s_i and n_i are the selection coefficients and number of molecules of species i . In a known mixture of solutes, s_i for the individual components can be calculated with the help of eq. (1) from the experimental and theoretical molecular weights, as shown in Table III, while the quantity n_i can be varied for two or more solutes.

TABLE III
Experimental and Theoretical Molecular Weights of Polystyrenes

Sample	Reported		Number-average molecular weight			
	\bar{M}_n	\bar{M}_w/\bar{M}_n	Mem-brane B-20	Mem-brane B-19	Mem-brane B-18	$(S_2^2)^{1/2}$, A.
P.S. 05	696,000	<1.05	243,000	530,000	729,000	362
S-105	147,000	<1.06	142,000	145,000	145,000	170
S-102	78,000	<1.06	78,000	79,900	85,800	125
7a	50,100	<1.06	50,293	56,000	59,000	98
2a	19,800	<1.06	18,819	25,365	34,726	49
8a	10,300	<1.06	9,440	13,022	29,170	41
11a	4,000	<1.06	3,670	4,994	30,867	20

A plot of S obtained with the most permeable membrane (B-18) for all the polymers, listed in Table III versus both their true and experimental molecular weights is found in Figure 4. It shows that S increases rapidly as the divergence of the experimental from the theoretical molecular weight decreases with increase in molecular weight.

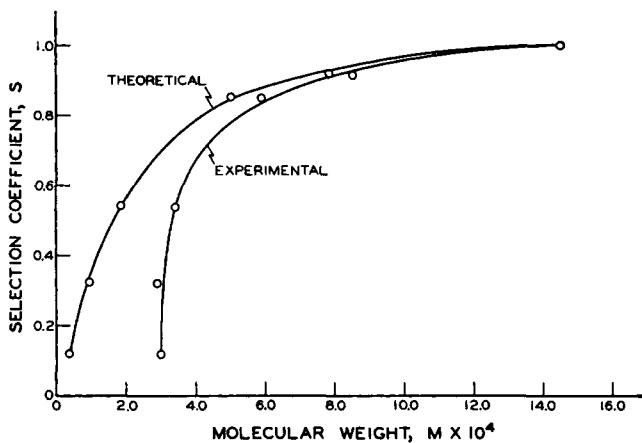


Fig. 4. Variation of selection coefficient S with theoretical and experimental (on membrane B-18) molecular weights for the single solutes.

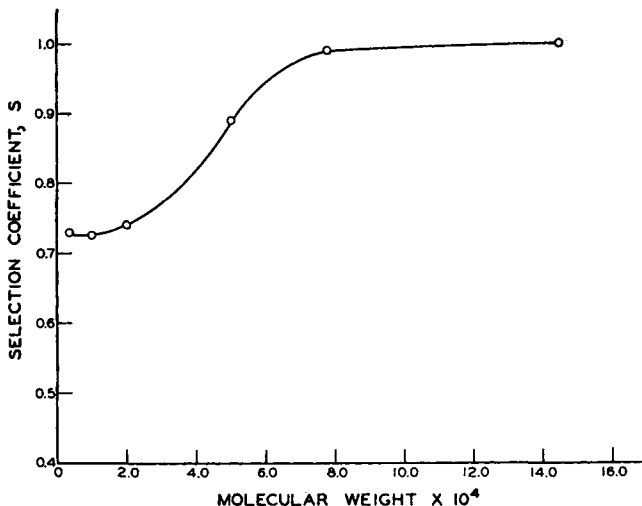


Fig. 5. Variation of selection coefficient S with the experimental molecular weight for the single solutes determined on membrane B-19.

The relation between S and M in Figure 4 is not sigmoidal as theorized by Staverman,⁵ apparently because the points on the curve represent single solutes of narrow distribution rather than portions of a random distribution of molecular sizes.

A sigmoidal relation for single solutes with the medium B-19 membrane has been found, as is seen in Figure 5. The lowest value of S in this case is 0.730. It is evident that both the pore size distribution in the membrane and the molecular weight distribution of the polymers influence the nature of the S_n versus \bar{M}_n curves.

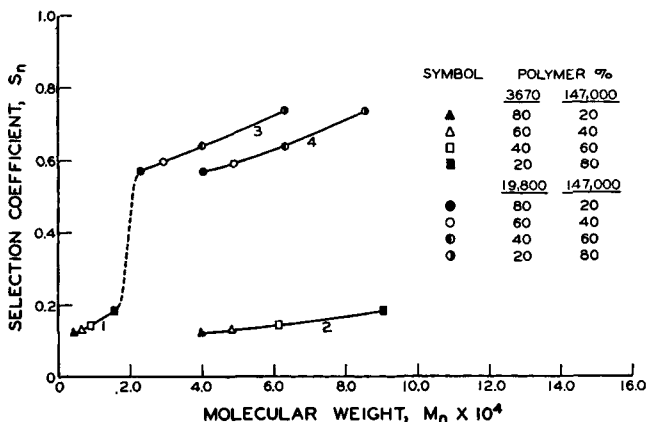


Fig. 6. Variation of selection coefficient S with the theoretical and experimental (on membrane B-18) molecular weights of mixed solutes.

To determine the selectivity of the mixed solutes $\bar{M}_n = 147,000$ was mixed in varying proportions with $\bar{M}_n = 3,670$ and with $\bar{M}_n = 19,000$ and measured in the least dense membrane B-18. The theoretical molecular weights were calculated from the relation

$$\bar{M}_n = \frac{\sum m_i n_i}{\sum n_i} \quad (3)$$

and the S_n values were obtained from eq. (2).

Figure 6 shows the relation between S_n and the true molecular weight calculated from eq. (3) for the mixtures. The dotted portion of the curve was obtained with eqs. (2) and (3) for mixtures of suitable proportions. The curve is sigmoidal representing more nearly the random case. Figure 6 also shows S_n obtained from the experimentally determined \bar{M}_n by means of eq. (1), and the relation between S_n and the experimental molecular weight. The S_n values obtained in the two ways are seen to be closely similar.

RESULTS AND DISCUSSION

Apparent Molecular Weights Determined with Three Membranes

The molecular weights of the polystyrenes reported by the suppliers and determined by us with the three membranes are given in Table III.

It is seen in Table III that the densest membrane, B-20, gave the expected molecular weight for all the samples except the high molecular weight sample $\bar{M}_n = 696,000$. In a static osmometer, several days and even weeks could be required¹² for equilibration of a solute of high molecular weight with such a dense membrane. When the measurement begins in the present instrument, the solvent reservoir drops to restrain the upward movement of solvent and bubble. Since the membrane is also reluctantly permeable to the solvent, time does not allow the reservoir to rise to the

required extent during the short period of measurement and a falsely high pressure and low molecular weight are obtained. Undoubtedly equilibrium is also incomplete when lower molecular weight samples are measured in the densest membrane but the systematic error is smaller compared to the higher pressure in the case of smaller molecules. Based on the reported data the error is not greater than 2% for a molecular weight of 145,000 and about 1% for a molecular weight of 3670. The nonequilibrium condition is also responsible for the low value obtained with the $\bar{M}_n = 696,000$ sample when the medium B-19 membrane was used.

In the densest B-20 membrane, selectivity effects are absent, and true molecular weights below 4000 are obtained with this membrane as was also reported by Feist.¹⁶ It is estimated that the nonequilibrium condition restricts the upper limit for this membrane to about 300,000. Both selectivity and nonequilibrium effects are present in measurements with the medium-porosity (B-19) membrane, and the limits of accurate determination are estimated from Table III to lie between about 90,000 and 500,000. In the most porous membrane the Staverman selectivity effects are greatest, and accurate values for polystyrene are not obtained below a molecular weight of 145,000. There is no limit at the other end of the molecular weight scale as equilibrium is easily obtained with the most porous membrane.

It cannot be expected that the B series membranes of this number will always perform within similar molecular weight limits, since it was observed that the membranes become less porous with time in storage. This occurred both in storage at 5°C. in 20% ethanol to which formaldehyde was added and in the toluene solvent. The B-18 membrane was used during a 6-month period after purchase with no evident change in porosity. The B-19 membrane, however, used 10 months and again 13 months after storage was found to have become appreciably more dense in the 3-month interval. The densest membrane, B-20 was in storage for two years before use in this study and may be considerably more dense than would be a newly purchased membrane of this number.

The relative molecular weight limit for a membrane may be estimated from the time required to reach a constant reading with solvent on both sides of the membrane as given in Table I. If equilibrium is obtained quickly the membrane is probably suitable for high molecular weight samples while long equilibration times reflect dense membranes suitable for lower molecular weight samples. Since the measurement can be made quickly it is safest to compare molecular weights obtained with different membranes to see if selectivity or nonequilibrium effects are present.

To obtain an estimate of the size of the diffusible molecules in terms of the selectivity of the membranes, radii of gyration of the polymers are given in Table III. Their calculation is based on the Porod-Kratky persistence length¹⁷ obtained from the viscosity equations of Eizner and Ptitsyn¹⁸ for polystyrene in benzene.¹⁹ The Benoit-Doty equation²⁰ $(S_z^2)^{1/2} = a^2(Nb/3a - 1)$ for the monomolecular case is used to obtain

the radius of gyration where a , the persistence length is 20.4 Å., b the monomer length is taken as 1.54 Å., N is the DP, and the monomer weight is 52.1. It will be recalled that polystyrene occupies a small volume in solution compared to cellulose derivatives, which were found¹⁹ to have persistence lengths of *ca.* 56 Å. and radii of gyration nearly three times as great as polystyrene at a given DP.

CONCLUSIONS

The characteristics of the Mechrolab rapid osmometer which has a small constant volume on the solvent side of the membrane, coupled with the use of a range of narrow distribution polymers and uniform membranes has made it possible to obtain an exhaustive measure of the effects of diffusion, Staverman selectivity, and of nonequilibrium with three membranes commonly used in osmometry.

It has been shown that equilibrium is not attained with the two densest membranes in the rapid measurement. While this causes little error for low molecular weights where the pressures are high, the error is great when the molecular weight is high and the total pressure is low.

As a result of nonequilibrium effects the densest membrane has an upper molecular weight limit of about 300,000 and the medium membrane an upper limit of about 500,000 while the grossest membrane has no upper limit which results from membrane effects. Staverman selectivity effects, on the other hand, restrict measurement at the lower end of the molecular weight scale so that the medium membrane does not give true values of linear polystyrene below a molecular weight of about 90,000 and true values below about 145,000 are not obtained with the grossest membrane. Accurate values as low as 3670 can be obtained, however, with the densest membrane for which no apparent selectivity effects were found.

Enormous selectivity effects were found in the grossest membrane when mixtures of diffusible and nondiffusible polystyrene were determined and theoretical values of the selectivity coefficient S_n were confirmed experimentally. Diffusion effects could be largely overcome when the pressure reading was made quickly enough but selectivity effects are in no way ameliorated so that calculated molecular weights can be grossly in error if diffusible molecules are present. If the reading is not taken immediately when diffusion is present the effect is great although the amount diffused is small, since only one per cent need diffuse in the instrument to obtain a like concentration on the solvent side.

When realistic estimates of the hydrodynamic volume of other polymers in comparison to polystyrene become available, choice of the proper membrane may be made from volume data such as that given in Table III. The ease with which membrane porosity effects on osmometry can be studied suggest that sorption and other membrane phenomena could also be readily followed with the instrument.

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