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OSMOMETRY WITH MEMBRANES PERMEABLE TO SOLVENT AND SOLUTE

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NEGATIVE REFLECTION COEFFICIENTS

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ANOMALOUS OSMOSIS RESULTING FROM PREFERENTIAL ABSORPTION

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OSMOMETRY WITH MEMBRANES PERMEABLE TO SOLVENT
AND SOLUTE³.

Osmometry with Membranes Permeable to Solvent and Solute³.

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According to theoretical considerations of Staverman² the molecular weight of a substance can be determined by means of osmometry even when the membrane is permeable to the solute of which the molecular weight must be determined. In this case the reflection coefficient of the membrane for the solute must be determined separately. The feasibility of the method is demonstrated by a molecular weight determination of sucrose from osmometry with membranes highly permeable to sucrose.

Osmometry is a simple and sensitive method for molecular weight determinations. For the determination of number average molecular weight of hetero disperse high polymers it is the only exact method of sufficient accuracy.¹ However, experimentally there are various difficulties. One of the most critical difficulties is that membranes of sufficient permeability to transmit solvent with sufficient speed generally also transmit solute molecules. Staverman² proposed to overcome this difficulty by measuring the permeability of the solute in a separate experiment and taking the permeability thus found into account in calculating the molecular weight from the apparent pressure P^* , experimentally measured as the pressure at which the net volume flow through the membrane vanishes.

The quantity characterizing the permeability of the solute is the reflection coefficient σ , defined by

$$1 - \sigma = \tau_1/c_1. \quad (1)$$

τ_1 is the mechanical transport number of the solute (component 1); this is the volume fraction of solute in the liquid passing through the membrane in a permeation experiment; c_1 is the volume fraction of the solute in the solution. When the membrane is equally permeable to solvent and solvent $\tau_1 = c_1$ and $\sigma = 0$, no solute is reflected by the membrane; when the membrane is ideally semipermeable $\tau_1 = 0$ and $\sigma = 1$. Staverman has shown that once σ is known, the true osmotic pressure Π can be calculated from σ and P^* by the simple equation

$$\sigma\Pi = P^*. \quad (2)$$

The reflection coefficient may be obtained by an experiment in which a measured volume of solution is passed through the membrane, beginning with equal volume fractions (i.e., equal concentrations) at both sides. After some time both the volume v and the volume fraction c will have changed, say, in cell α , from v to v' and from c to c' respectively.

Although one might expect that $c' > c$ if $v' < v$, we show in two subsequent papers that this need not hold generally. In any case, for an infinitesimally small transport of solution through the membrane (where $v' - v = dv$, $c' - c = dc$ and, hence, where

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the change in partial volume of solute in cell α is $v'c' - vc$) the definition of the mechanical transport number of solute is

$$\tau_1 = \frac{v'c' - vc}{v' - v} = \frac{(v + dv)(c + dc) - vc}{dv} = c \left(1 + \frac{d \ln c}{d \ln v} \right). \quad (3)$$

From (1) it follows that

$$\sigma = -d \ln c / d \ln v. \quad (3a)$$

If σ does not strongly depend on c , this may hold for finite transports of volume as well, so that after integration

$$\sigma = -\frac{\ln c'/c}{\ln v'/v} = \frac{\ln c'/c}{\ln v/v'}. \quad (4)$$

Although c and c' denoted volume fractions of solute, substitution of concentrations in weight per volume is justified in eqn. (4), unless the partial molar volume of solute varies to an unusually high degree. Once σ is known, the molecular weight can be determined from measurement of the apparent osmotic pressure from

$$M^{-1} = RT \lim (\Pi/c) = RT \lim_{c \rightarrow 0} (P^*/\sigma c). \quad (5)$$

As, during the experiment, solute permeates through the membrane into the solvent cell, the quantity measured is generally not P^* but ΔP^* which obeys (instead of (2)) the equation

$$\Delta P^* = \sigma \Delta \Pi, \quad (2a)$$

so that

$$M^{-1} = RT \lim_{(c_\alpha + c_\beta) \rightarrow 0} (\Delta P^*/\sigma \Delta c). \quad (5a)$$

Information about permeability coefficients, as well as the mol. wt., is derived from our measurements on aqueous sugar solutions.

From the decay of Δc during measurements with zero total volume flow, the solute transport J_1^* can be calculated. We define $J_1 = v_1 \dot{n}_1$, where \dot{n}_1 is the number of solute molecules passing the membranes, and v_1 the molar volume of the solute component. We then have

$$J_1^* = v_1 \sum_k L_{ik} (v_k \Delta P + \Delta \mu_k^c) \quad (\text{with } \sum_k v_k J_k^* = 0), \quad (6)$$

where L_{ik} are the permeability coefficients as used by Staverman and $\Delta \mu_k^c$ is the difference in chemical potential between the two compartments of the osmometer.

Introducing into (6) the following equations,

$$\begin{aligned} \Delta P &= \Delta P^*; \quad \Delta \mu_0^c = -v_0 \Delta \Pi; \\ \Delta \mu_1^c &= -(n_0/n_1) \Delta \mu_0^c = (\phi_0/\phi_1) v_1 \Delta \Pi; \\ L_{01} &= L_{10}; \quad M_{ik} = v_i v_k L_{ik}, \end{aligned}$$

and eqn. (2a) we obtain

$$J_1^* = (M_{01} + M_{11}) \Delta P^* - \left(M_{01} - \frac{\phi_0}{\phi_1} M_{11} \right) \frac{\Delta P^*}{\sigma}, \quad (7)$$

where ϕ_i is the volume fraction of component i .

In an ultra-filtration experiment ($\Delta \mu_i = 0$), two quantities are measured simultaneously, the total volume flow

$$J_v = \sum_k v_k J_k = \sum_i \sum_k M_{ik} \Delta P = (M_{00} + 2M_{10} + M_{11}) \Delta P, \quad (8)$$

and the reflection coefficient σ given in (4). From the definition of the reflection coefficient (eqn. (1)) the following relation is derived between σ and the coefficients M_{ik} :

$$1 - \sigma = \frac{\phi_0 \left(\frac{J_1}{J_v} \right)_{\Delta\mu=0}}{\phi_1} = \frac{M_{10} + M_{11}}{\Sigma \Sigma M_{ik}} \frac{\phi_0}{\phi_1} \quad (9)$$

Thus by measuring the total permeability, the reflection coefficient and the solute flow J_1^* at $J_v = 0$, the three coefficients M_{ik} can be derived from eqn. (7), (8) and (9). Additional measurement of ΔP^* allows one to calculate the molecular weight from (5a).

EXPERIMENTAL

OSMOMETERS

Fig. 1 shows our type of osmometer. The membrane consists of a bag-shaped piece of Vycor glass on which two ground-glass joints are coaxially mounted; the outer one (a ball joint) fixes the pressure chamber and provides a beaker for the mercury lock which must prevent leakage of solution through the inner ground-glass joint fixing the capillary. Both cells are provided with a stirrer, actuated by one coaxially rotating permanent magnet under the beaker. We found that neglect of efficient stirring may result in observed values of ΔP^* which are more than 10 % too low. Through the double wall of the beaker, water from a thermostat can be pumped. In order to correct for the remaining thermal effect the temperature can be read on a Beckmann thermometer placed in the outer cell.

As the liquid comes only in contact with glass, mercury, Teflon and air or nitrogen gas, the osmometer can be used for a great variety of solutions. The apparatus can be cleaned thoroughly and frequently by washing it with fuming nitric acid since micro-organisms appeared after a week with the membrane in the sugar solution. Because of the rigidity of the Vycor glass there was only a negligible ballooning effect up to pressures of $2\frac{1}{2}$ atm. The pressure difference, regulated by manostats, between the two cells could be varied by nitrogen gas in the pressure chamber.

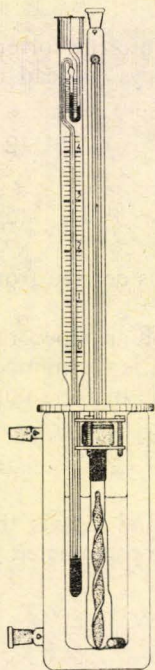


FIG. 1.—Osmometer with Vycor glass membrane and stirrer; height 55 cm.

MEASUREMENT OF $\Delta P^*/\Delta c$

Knowledge of ΔP^* is only of interest if we know the concentration difference Δc at the same time. We can measure the concentration in the inner cell only at the moments of filling and of dismounting, so that Δc too is only known at these times. On the other hand, there must be a finite lapse of time between filling and the first measurement of ΔP^* (because of temperature heterogeneity, drainage in the capillary, etc.) and between the last measurement of ΔP^* and dismounting. That means that we have to measure the continuously diminishing values of $\Delta P^*(t)$ several times and to extrapolate these observations in both directions to get two values $\Delta P^*/\Delta c$ from one experiment.

The simplest way to determine ΔP^* is to observe the spontaneous rising meniscus until it comes to a temporary standstill, after which it begins to fall. It is advantageous to establish with the aid of nitrogen gas, a constant overpressure ΔP only slightly lower than the momentary value of ΔP^* . After the meniscus has reached its maximum height, the overpressure is reduced by an adequate amount and the next measurement of ΔP^* , now lower, can be performed.

This "static" method has the disadvantage that it may take a considerable time, especially at low Δc , before a convincing maximum in the height against time curve becomes apparent. This results in an accurate value of ΔP^* at a not very accurately known time. Therefore we preferred "dynamic" measurements, in which at several constant overpressures, some of them higher and others lower than ΔP^* , the successive volume fluxes are determined and the pressure difference at which the flux would have been zero, i.e., ΔP , is found by interpolation. The fact that ΔP^* diminishes continuously during the finite time of measurement, introduces an inaccuracy in this interpolation, which can, however, be eliminated. To that end we divide the time into a number of equal periods, during which we measure the fluxes alternately at one fixed overpressure higher and at one lower than ΔP^* . The average value of ΔP^* during the period p is found then by intersection of the line connecting the measured flux during p and the geometric mean of the measured fluxes at $p-1$ and $p+1$ with the pressure axis, as seen in fig. 2.

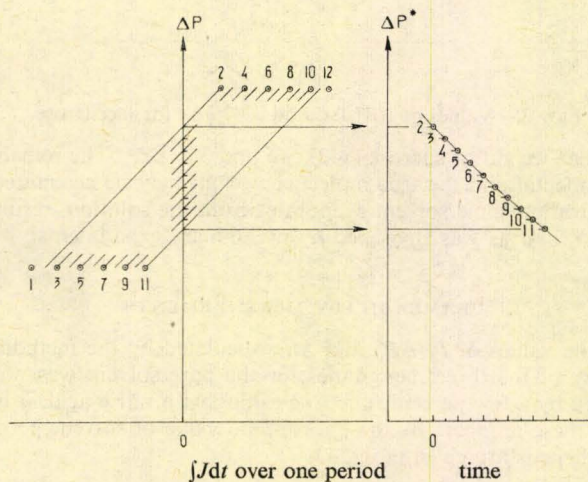


FIG. 2.—Dynamic measurement of ΔP^* .

In our experiments with sugar solutions $\log \Delta P^*(t)$ against time proved to be a linear function which made extrapolation of the observed $\Delta P^*(t)$ to the time of known Δc easy.

MEASUREMENT OF σ

The initial volume v (approx. 15 ml) of the inner cell was determined by filling it with the aid of a calibrated burette. The final volume v' was calculated from the previously determined permeability of the solution, the duration of ultrafiltration and the pressure difference exerted. The change in concentration after ultrafiltration was determined with the aid of a Zeiss-Rayleigh interferometer. With a permeability of approx. 30 mm³/h atm, a selection coefficient of approx. 0.2 and a pressure difference of 2½ atm, ultrafiltration took approx. 20 h for a 2% change in concentration.

RESULTS

MOLECULAR WEIGHT OF SUGAR

In fig. 3 the values of $\Delta P^*/\Delta c$ measured for three membranes A, D and E give the lower series of points. From the intercept $(1.38 \pm 0.02) \times 10^{-2}$ L atm/g we calculate the apparent molecular weight to be 1760. Above this series of $\Delta P^*/\Delta c$ values are written the values for σ , found at several concentrations. Clearly there is no systematic dependence $\sigma(c)$, nor is there much difference in quality between the three membranes. $\Delta P^*/\sigma\Delta c$ is given by the upper collection of points in fig. 3.

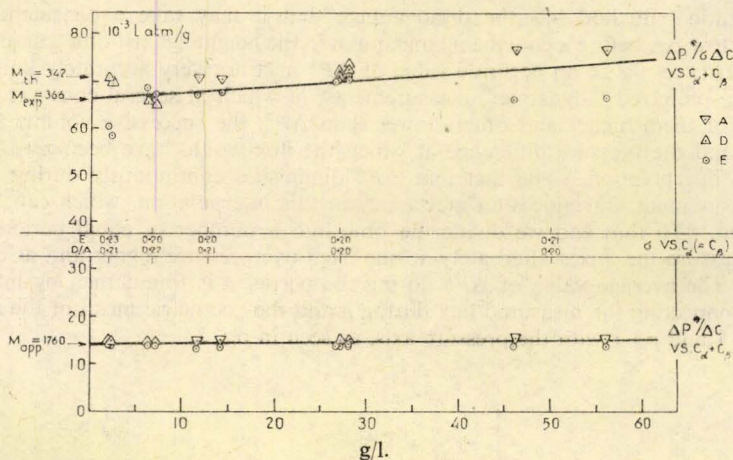


FIG. 3.—Values of $\Delta P^*/\Delta C$ and $\Delta P^*/\sigma\Delta c$ for saccharose.

For the molecular weight of sucrose (342), we find 366 ± 7 . The remaining discrepancy between the experimental and the true molecular weight may be accounted for by the fact that during ultrafiltration some solvent evaporates from the solution, resulting in a systematic error of 5-10 % in σ as was suggested by preliminary experiments.

PERMEABILITY MEASUREMENTS

Table 1 gives the values of $J_1^*/\Delta P^*$ and M_{ik} calculated by the method outlined above. As the permeability of the three membranes for the pure solvent was not the same, and, moreover, increased by a few percent, due to cleaning with nitric acid, it is better for comparison, to divide these numbers by the appropriate value of solvent permeability $M_{00}(0)$. These relative coefficients are given in fig. 4.

TABLE 1.—VALUES (in $\text{mm}^3/\text{h atm}$) OF $J_1^*/\Delta P^*$ AND THE COEFFICIENTS M_{ik} FOR AQUEOUS SUGAR SOLUTIONS AND POROUS VYCOR GLASS AT SEVERAL AVERAGE CONCENTRATIONS \bar{c} (in g/l.)

mbr.	\bar{c}	$J_1^*/\Delta P^*$	M_{00}	M_{01}	M_{11}
D	0.977	3.5	31.5	0.016	0.0005
E	0.976	4.0	33.8	0.016	0.0005
D	3.244	4.1	31.0	0.048	0.002
E	3.241	4.4	33.2	0.051	0.002
A	6.392	3.8	29.0	0.089	0.003
E	6.371	4.6	33.8	0.103	0.004
D	13.696	4.0	29.4	0.192	0.008
E	13.660	4.2	31.4	0.205	0.009
A	25.571	3.5	26.8	0.331	0.016
E	25.511	4.4	31.1	0.380	0.020

TABLE 2.—RELATIVE PERMEABILITY OF VYCOR MEMBRANES FOR AQUEOUS SUGAR SOLUTIONS

conc. g/l.	rel perm.	η_0/η
1.925	0.994	0.995
6.522	0.980	0.983
12.585	0.964	0.968
26.986	0.922	0.932
50.070	0.849	0.876
280.111	0.35	0.410

The relative permeability of the membranes for solution as a whole, $\Sigma \Sigma M_{ik}/M_{00}(0)$, proved to be slightly less than the (reciprocal) relative viscosity of the solution as may be seen in table 2.

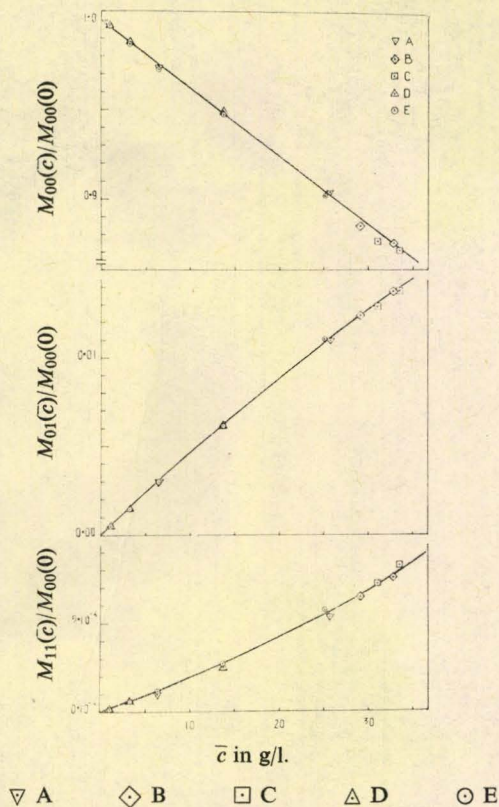


FIG. 4.—Concentration dependence of M_{ik}/M_{00} .

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¹ Bonnar, Dimbat and Stross, *Number-average Molecular Weights* (Interscience, New York, 1958).

² Staverman, *Recueil*, 1952, **71**, 623; *Trans. Faraday Soc.*, 1952, **48**, 176.

³ Talen, J. L., *Thesis* (Leiden, 1963).