A New Method of Determining Small Osmotic Pressures

II. Measurements and Results

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Measurements with an interference osmometer are reported. A dynamic technique has been consistently used. A detailed description of the sequence of operations is given. Different polymer — solvent systems have been examined; diagrams are shown and the time for and the accuracy of the measurements are discussed.

In an earlier paper¹ an interferometric method of measuring small differences in liquid levels with an accuracy of 1—2 μ was described. For some time now osmotic measurements on different polymer — solvent systems have been performed in this apparatus. The largest source of error in osmometry, however, seems to be the membranes, the influence of which on the measurements is very little understood. In spite of this, osmometry is an indispensable tool of high polymer chemistry and it is of great importance to develop methods which can facilitate work in this field.

Although this type of apparatus can be used for any kind of osmometry, it is particularly well suited for dynamic measurements. The sensitivity of the interferometric system makes it possible to accurately determine the rate of flow through the membrane even when working near to the equilibrium position. The cell (of Fuoss-Mead pattern) is of the "dynamic" type and the apparatus is on the whole convenient and quick in operation. It has therefore been considered to be of interest to devise a dynamic technique which would provide rapid measurements of satisfactory accuracy.

The chief advantage of a dynamic method in comparison with a static one is the relative rapidity with which measurements can be carried out. Problems in connection with osmometry with special emphasis on dynamic osmometry have been extensively discussed in a series of papers by Staverman^{2,3}. Among the dynamic methods in use the one introduced by Gee⁴ and Montonna and Jilk⁵ has been found to be most convenient for this apparatus.

Suppose that during the time dt a volume of liquid dV passes through the membrane. If π is the equilibrium position, *i.e.* the difference between the

menisci at osmotic equilibrium, and h denotes an arbitrary difference in menisci levels, $\frac{dV}{dt}$ is assumed to be proportional to the difference $(h-\pi)$ and we obtain

$$\frac{dV}{dt} = k_1 (h-\pi) \quad (1)$$

But as the tubes in the manometer are cylindrical

$$dV = k_2 dh \quad (2)$$

Thus

$$\frac{dh}{dt} = K (h-\pi) \quad (3)$$

where

$$K = \frac{k_1}{k_2} \quad (4)$$

Now if $\frac{dh}{dt}$ is determined at different positions h and plotted against h , a straight line is obtained from which the value of h at $\frac{dh}{dt} = 0$ can be found, i.e. $h = \pi$. The factors governing a possible deviation of this "dynamic" value from the "thermodynamic" value are the properties of the membrane (porosity, elasticity and thermodynamic stability), the mode of measuring and the accuracy of the rate determination. Together with other experimental errors — with the exception of factors giving rise to systematic deviations — this may appear as a dispersion of the points in the $\frac{\pi}{c}$ — c plot.

As pointed out by Staverman^{2,3} it is very important not to have any diffusion of polymer through the membrane even if a "quick" dynamic method is applied. Although a fairly porous membrane has been used in the work reported here none or extremely small diffusion of solute has been detected. This was achieved by checking the constancy of the equilibrium position over a long time (several days) for one solution of each fraction examined. The usual control of the solvent side after the measurements by pouring an excess of precipitant into the contents of the cell was also made. In no case did turbidity arise.

For the following description of the sequence of operations the reader is referred to Fig. 1 in the preceding paper¹.

The membrane was conditioned from one solvent to another in the usual manner by the successive increase of the amount of new solvent in mixtures of new and former solvent. In cases where the two solvents were not miscible in all proportions a suitable intermediary solvent was used. Throughout this work it was found that, for the type of membrane used (Ultracellafilter), this procedure of conditioning must be extended over a period of at least one week. When treated in this way the membranes showed a small and satisfactorily reproducible "cell constant" (see below).

After the initial filling of the cell any air bubbles remaining were removed by rapidly sucking a large amount of degassed solvent through both halves of the cell. A quantity of liquid was then sucked off such that the menisci were situated in the glass capillaries which were held by means of the springs in such a position as to give a suitable level in M.

The reference position was now determined with solvent in both halves of the cell. Using LC (in steps of 0.5 mm) and SR (with fixed SL) the fringes were located. The levels were then adjusted to positions desired, usually in intervals of 0.5 mm, by pipetting calculated amounts of solvent into the flasks (at II) without introducing air bubbles into the cell. For each level difference h the rate of flow $\frac{dh}{dt}$ was determined from the movement of the interference fringes during a suitable time, usually 10 mins. Generally, only two readings on SR were made, one at the time $t = 0$ and one at $t = 10$. The rate values could of course be smoothed out by taking readings at closer time intervals (*e.g.* every minute) but this is fairly tiring and does not improve the interpolation accuracy essentially. The readings on LC and SR give h and $\frac{dh}{dt}$ respectively:

If h_1 = reading on LC (in mm or in number of fringes of wavelength λ_D)

h_0 = reading on SR at the time $t = 0$

h_t = reading on SR at the time $t = \Delta t$

$$\Delta h = h_0 - h_t$$

$$\text{one has } \begin{cases} h = h_1 + h_0 - \frac{\Delta h}{2} \\ \frac{dh}{dt} = \frac{\Delta h}{\Delta t} \end{cases} \quad \begin{matrix} (5) \\ (6) \end{matrix}$$

The magnitude of $|\Delta h|$ is very small, between 1—4 % of h .

The next step was to fill the cell with the solution. All solutions were prepared by weighing from stock solutions. Specially designed flasks were used for this purpose. By means of a simple glass arrangement the required amount of stock solution was, under pressure from a rubber bulb, transferred into the weighing flask where dilution was carried out. In exactly the same manner the solution was transferred to the flask on the osmometer (at II). In this way changes in concentration due to evaporation (while handling the solutions) were avoided. This was very important as the concentrations were not measured afterwards (see below).

Because of the design of the cell the process of exchanging solvent was a somewhat delicate matter. The fairly large volume of solution (at least 100 ml) which is required must be passed very slowly through the cell chamber before reproducible measurements can be made. The rate of flow of solution through the cell was controlled by varying the amount of solution in the osmometer flask, the level in M being kept approximately constant during the exchange. The time required for this part of the operation was generally about one hour.

The sensitivity of the interferometric system was such that it was a relatively easy matter to find an approximate equilibrium position (within 0.2—0.3 mm) shortly after the cell was filled and the system was left for thermostating for about half an hour. Rate determinations were then made, as described above, on both sides of the equilibrium position. This procedure was repeated for all the solutions.

It was mentioned above that the concentrations of the solutions were determined before the osmotic measurements. This was done because for many reasons an accurate evaluation afterwards is difficult and would probably be

of doubtful significance (see *e.g.* Grassie⁶). Apart from possible evaporation during the transfer of solutions, error in this variable could arise from the passage of solvent through the membrane and from a possible adsorption of solute on the membrane. The amount of solvent passing through the membrane during thermostating is small and is estimated to be less than 0.5 % of the cell volume. If there is an appreciable adsorption on the membrane its influence on the concentration is considerably reduced or even eliminated by the following facts: a) the membrane was in contact with the solution during the time of exchange (about one hour) which makes it very probable that the membrane was saturated with solute when the measurements on the last part of the solution in the cell were started, b) measurements were made on solutions of increasing concentration.

The membrane which has been in continuous use for about half a year without any inconveniences was an Ultracellafilter from Membranfiltergesellschaft, Göttingen, labelled 30. The constant K (eq. 3) may be used to characterize its permeability or perhaps better the quantity τ defined as

$$\tau = \frac{\ln 2}{K} \quad (7)$$

τ varies slightly with the solvent (*cf.* Breitenbach and Forster⁷). The whole membrane area gives a value of τ between 3 and 4 hours in our apparatus and for the solvents used. This means that if π is to be found statically and if the initial positions of the menisci differ from the equilibrium positions to the extent say, 0.1 mm which is in practice very difficult to achieve in a short time, it will take between 12 to 15 hours before π can be determined with an accuracy of 0.01 mm. By applying the dynamic technique, a rate determination at one position of the menisci could be carried out in 10 to 20 mins. and since measurements were generally made at four positions for each concentration and as the exchange of the solution and thermostating as mentioned above required about two hours a $\frac{\pi}{c}$ — c diagram containing data for four or five concentrations could be obtained within two days.

Fractions of three different kinds of polymers were examined. They covered a range of molecular weights from about 100 000 to 3 000 000. Methyl ethyl ketone (MEK) and ethyl acetate (Et Ac) were used as solvents. The samples are described as follows:

CNF—S, a cellulose nitrate fraction *, prepared by fractional precipitation in the system acetone-water. Molecular weight about 100 000. Nitrogen content: 12.40 %. Solvent: MEK.

PSF—12, a polystyrene fraction, prepared by fractional precipitation in the system carbon tetrachloride-methanol. The polymer synthesized by emulsion polymerisation. Molecular weight about 250 000. Solvents: MEK and Et Ac.

PSF—III, a polystyrene fraction, described in "Report on Molecular Weight Measurements of Standard Polystyrene Samples"⁸. Molecular weight about 500 000. Solvent: MEK.

* The author is indebted to fillic. Y. Sahlman for this sample.

Table 1. Experimental results for different samples in methyl ethyl ketone (MEK) and ethyl acetate (Et Ac)

Sample	Solvent	$c \cdot 10^3$ g/ml solution	π mm solution	$\frac{\pi}{c} \cdot 10^{-4}$ dyne g ⁻¹ cm
CNF-S	MEK	0.0462	1.20	20.6
		0.0983	2.70	21.7
		0.148	4.25	22.6
		0.231	7.39	24.9
		0.378	14.16	29.5
PSF-12	MEK	0.0367	0.47	9.9
		0.0667	0.85	10.1
		0.136	1.87	10.8
		0.172	2.33	10.8
		0.207	2.82	10.7
		0.294	4.07	10.9
		0.312	4.18	10.6
		0.350	4.95	11.2
PSF-III	MEK	0.479	7.03	11.6
		0.0939	0.59	5.00
		0.190	1.19	4.95
		0.286	1.81	5.01
		0.428	3.10	5.72
PMF-EI	Et Ac	0.566	4.57	6.40
		0.0419 *	0.69	14.8
		0.0825 *	1.39	14.9
		0.119	1.98	14.6
		0.211	3.64	15.2
PSF-12	Et Ac	0.294	5.26	15.8
		0.0743	0.86	10.2
		0.102	1.20	10.5
		0.108	1.28	10.5
		0.225	2.64	10.4
PMF-EII	Et Ac	0.345	4.25	10.9
		0.236	0.37	1.4
		0.293 *	0.58	1.8
		0.310 *	0.56	1.7
		0.407	1.01	2.2

* Static measurements.

PMF-EI and *PMF-EII*, two polymethylmethacrylate fractions * prepared by fractional precipitation in the system acetone-methanol. The polymer synthesized by block polymerisation. Molecular weights about 200 000 and 3 000 000. Solvent: Et Ac. All samples were dried to constant weight at elevated temperature (about 50° C) in vacuum. The solvents have been made free from water and purified by distillation. Refractive indices: MEK : n_D (25° C): 1.3764; Et Ac : n_D (25° C): 1.3697.

* The author is indebted to fillic. F. Eriksson for these samples.

Table 2. Values of the constants in eqs. (8) and (9) and sedimentation molecular weights (UC)

Sample	Solvent	$\left(\frac{\pi}{c}\right)_0 \cdot 10^{-4}$ extrapolated	$B \cdot 10^4$	M osmot.	M UC
CNF-S	MEK	19.0	10.8	130 000	132 000
PSF-12	MEK	10.1	1.2	245 000	—
PSF-III	MEK	4.6	1.0	540 000	—
PMF-EI	Et Ac	14.4	1.9	172 000	182 000
PSF-12	Et Ac	10.2	0.7	243 000	—
PMF-EII	Et Ac	0.8	1.2	3 100 000	2 100 000

All measurements were carried out at 25.00° C. All experimental data have been treated and constants computed in accordance with the equations

$$\begin{cases} \frac{\pi}{c} = RT (A + Bc + \dots) & (8) \\ A = \frac{1}{M} & (9) \end{cases}$$

All units and symbols used here are those recommended in "Report on Nomenclature in the Field of Macromolecules"⁹.

Tables 1 and 2 give a survey of the experimental results and of the constants calculated from eqs. (8) and (9). Table 2 also includes some data from sedimentation and diffusion measurements. Figs. 1 and 2 show the corresponding $\frac{\pi}{c} - c$ plots, where open circles indicate dynamic and filled circles static measurements the latter having been made in a few cases for comparison. Fig. 5 in the preceding paper¹ is a typical rate diagram with the corresponding $\frac{\pi}{c} - c$ plot.

The concentrations are given in g/ml solution but were originally determined in g/g solution and converted into the former unit using the density of the solvent*.

For $\frac{\pi}{c}$, however, the same value is obtained whether π is expressed in cm solution and c in g/g solution or π in g/cm² and c in g/ml solution. It has not been considered necessary to apply any special corrections (see *e.g.* Lang¹⁰) to the data. It might also be mentioned here that the difference in refractive index between solvent and solution in the concentration range used is so small that error due to this is far less than other experimental errors.

The dispersion of the points in the rate diagram is small and the dynamic equilibrium value can be interpolated with an accuracy of about ten fringes, *i.e.* between 0.02 and 0.01 mm. Within the limits of experimental error the

* No density measurements were carried out. For the conversion of the unit, density data of the solvents from international tables were used.

Fig. 1. $\frac{\pi}{c}$ — c relationship for cellulose nitrate (CNF) and polystyrene (PSF) fractions in methyl ethyl ketone.

lines are parallel; the slopes are the same for different polymers in the same solvent. There is, however, a tendency for the slope to decrease with increasing concentration, which might be explained by a diminishing "effective" membrane area with increasing amounts of polymer. The diagram also shows the sensitivity in the rate determination: the largest value of $\frac{dh}{dt}$ is 0.05 mm per 10 mins. It is not a coincidence that the extrapolated value for the reference position is zero. The screw SL was put in such a position as to give this value on the diagram. SL was of course not changed during the whole experiment. It corresponds in fact to a "cell constant" of about 0.05 mm. The reproducibility of the reference position was satisfactory. For this sample (PSF—III) it was checked immediately after the measurement on each solution and this is denoted in the diagram by the different sets of points.

In the $\frac{\pi}{c}$ — c plots (Figs. 1 and 2) all extrapolations to zero concentration have been made along straight lines and only slight tendencies for curvature upwards may be noticed in the relatively narrow concentration range in which

Fig. 2. $\frac{\pi}{c}$ — c relationship for polystyrene (PSF) and polymethylmethacrylate (PMF) c fractions in ethyl acetate. Filled circles denote static measurements.

these measurements have been performed. The uncertainty in the determination of π can be particularly studied in Fig. 1 for the fraction PSF—12 where data from measurements on nine different concentrations are plotted. Furthermore, this fraction was examined in two different solvents (see also Fig. 2) giving results of good agreement. The deviation of the points from the straight line is in no case larger than about 5% of the extrapolated $\frac{\pi}{c}$ value and this seems to be the upper limit of the dispersion of the data obtained in this investigation.

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