A New Method of Determining Small Osmotic Pressures

I. Principle and Apparatus

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The principles of an interferometric method of determining small pressure differences are discussed. An accuracy of $1-2\ \mu$ in the measurements can be obtained. An extensive description of the apparatus is given. It has been used for dynamic osmometry. Some experimental data from measurements on a polystyrene sample are reported.

In many physico-chemical methods the ability to measure small pressure differences is of great importance. This is particularly true in determinations of the osmotic pressure of solutions of macromolecules because all extrapolation procedures will become more certain and very large molecular weights can be determined more accurately. Further, very small changes in the difference of level between the menisci can be detected, thus making a dynamic method more reliable. As a rule, the menisci are observed in capillaries by means of cathetometers giving an accuracy of about 0.01 mm. Svedberg and Jullander^{1,2} introduced the osmotic balance which was modified and improved by Enoksson^{3,4} and Masson and Melville⁵. By this method of measurement it was possible to observe differences in menisci levels as small as 0.001 mm.

We have devised an interferometric method giving about the same accuracy as the osmotic balance. As the apparatus has proven to be simple and convenient in operation, a detailed description of it might be of interest. It has been in constant use for about two years and has been mainly used for the determination of osmotic pressures dynamically.

The basic idea behind the method is the interferometric determination of a difference in optical path. The principle has long been known and has been used by many scientists in various fields of research. In manometry the interferometric methods have been applied in different ways to obtain high accuracy. For example, a barometer of very high precision using the reflection of light beams from the mercury surfaces has been recently described⁶. In our case the organic solvents used for the solutions of polymers are also most conveniently used as the manometric liquid.

In designing the apparatus the chief aim was to obtain the greatest simplicity in construction and operation. It was thus considered expedient to make the optical arrangement as simple as possible and to try to reduce the number of adjustments to a minimum. This was accomplished by building the apparatus in such a way that the two light beams passed through the manometric liquid*.

If the two light beams of wavelength λ pass through two layers of length h with a difference in refractive index Δn , the basic formula is

$$h \Delta n = N_{\lambda} \lambda \quad (1)$$

where N_{λ} is the number of fringes of wavelength λ corresponding to the change $h \Delta n$ in optical path. Of course any one of the variables in (1) can be calculated if the other three are known. Since in our case h (see M in Fig. 1) denotes the difference in level between two menisci of the same liquid and $\Delta n = n - 1$ ** where n is the refractive index of this liquid, (1) becomes

$$h(n - 1) = N_{\lambda} \lambda \quad (2)$$

Here n , N_{λ} and λ will be known and consequently h computed. For the sake of simplicity white light is used. Essentially no difficulties arose from this.

One of the main problems was to find the most suitable diameter of the tubes where the light has to pass menisci, *i.e.* in M (Fig. 1), which will be called the manometer. Because of the curvature of the menisci it is advantageous to work with large diameters. The use of large diameters also has the great advantage that errors due to surface tension are reduced. From another point of view, it is not desirable to have a large distance between the two light beams since in our simple Rayleigh system the fringes will then be too close to each other. Furthermore, small changes of the levels due to flow of liquid through the membrane correspond to a fairly large volume of liquid in wide tubes. This results in a change of the concentration of the solution in the osmotic cell which is usually made to hold a small volume. We have found that in our system a diameter smaller than 20 mm is hardly possible. For practical reasons this necessitates a distance of 25 mm between the light beams. However, very clear and distinct fringes were obtained with most liquids, and it was possible to determine N_{λ} reproducibly (eq. 1) with an accuracy of one fringe⁷. This means that for most liquids, where $1.3 < n < 1.5$, the error will be 1–2 μ . A change in level of 0.1 mm corresponds to about 0.03 ml of liquid, this being less than 0.5 % of the volume of the cell (7 ml). As will be seen later⁸, it was not necessary to wait for such an amount to pass through the membrane before a final pressure could be determined. Furthermore, it may be observed that M is completely symmetrical and that the absolute positions of the menisci is of no importance. It was easy to thermostat the cell and manometer within a fairly wide temperature range. M is of course closed to prevent errors due to evaporation.

* Work with light beams reflected at the menisci is in progress at the Institute for other purposes where higher accuracy is required.

** More exactly, $\Delta n = n - n_1$, n_1 denoting the refractive index of the mixture of saturated vapour and air. $n_1 = 1$, however, is a very good approximation.

Fig. 1. Sketch showing the principle features of the apparatus.

A detailed drawing of the apparatus is shown in Fig. 1. The instrument can be divided into two main parts: (I) the manometer (interferometer) and (II) the osmotic cell. (I) is built on the stand of an upright drilling machine giving a rigid and stable support to the different units. These consist of the slit S , the lenses L_1 , L_2 , and L_3 , the glass compensator GC , the liquid compensator LC , and the manometer M . In the ocular L_3 , a cylindrical lense, the fringes are observed on a cross-wire CW . Since for practical reasons the optical system is made vertical, a mirror (not drawn in Fig. 1) is placed between L_2 and L_3 reflecting the light beams upwards in order to facilitate observation. It has been found necessary to use mirror, lenses and glass plates of good quality. L_1 is a "Rodenstock-Extra-Rapid-Aplanat" $1:7.7$ ($f = 400$ mm) and L_2 is a "Hilger quartz-glass-quartz triple objective" $1:3.5$ ($f = 1\,000$ mm). As concerns the glass plates the manufacturer gives the following guarantees: curvature $> 1\,000$ m, the angle between the two surfaces $< \pm 5''$.

Fig. 2 shows the glass compensator unit GC . It is entirely of conventional type and its description is merely given for the sake of completeness. The two compensating glass plates P_1 and P_2 (see also Fig. 1) are placed on holders in a

Fig. 2. The glass compensator (GC in Fig. 1).

brass tube to the upper end of which is attached a disc with a three point support for M. To the other end of the tube the lense L_2 is screwed. The angle of inclination of the glass plates can be varied by metal arms pressed by means of springs against micrometer screws SR and SL (Fig. 1). The readings are made on these micrometers. N_λ is obtained from a calibration of the readings in terms of the number of fringes of known wavelength. We used $\lambda_D = 589.3$ m μ . This calibration is made once and for all. The whole mechanical unit is fitted into the holder of the drilling machine table where also the micrometer screws SR and SL are fastened.

For various reasons⁷ (white light is used, dispersion correction, extension of the range of measurements) it is convenient to use a liquid compensator LC (Fig. 1) in combination with GC. It is essentially constructed as a micrometer screw fitted into a tube containing the liquid used as a solvent for the polymer under investigation. The geometrical path of the light beam through the liquid can be varied from 0 to 25 mm. The pitch of the screw (all metal parts in this unit are of stainless steel) was not accurate enough to be used for the localization of the fringes but it could be used in whole turns (*i.e.* every 0.5 mm) without any distortion of the image. The micrometer screw was calibrated by means of a microcomparator. It was of course necessary to use glass plates in the system and these are pressed against the bottoms of the tubes by means of nuts. Thin polythene films were used as packings. The liquid in LC was thermostated by water pumped through a jacket around the outer tube.

A detailed drawing of the manometer M is shown in Fig. 3. The cylindrical stainless steel block (1) contains the two manometer limbs (2) with a distance of 25 mm between their centres. They are closed at the bottom by a glass plate (4) tightened in a manner similar to that in LC (*i.e.* a metal plate (5) a nut (6), and a polythene washer). Two precision bore (20 mm) glass tubes are inserted into the manometer limbs with very good fitting. They are easily removed for occasional washing.

Fig. 3. Sketch of the manometer (M in Fig. 1).

On top of the block there are holders for glass plates. The latter have two functions: they prevent evaporation, and are of such thickness as to compensate exactly for the glass in LC. Tiny grooves under the glass plates ensure atmospheric pressure above the liquid in (2). M is provided with canals through which thermostated water is circulated and is covered with insulating material (3) having holes for the passage of the light beams.

The osmometer cell (II) (Fig. 1) is of a somewhat modified Fuoss-Mead pattern⁹. It is machined from silver blocks (containing about 17 % copper) which are clamped together by a frame of stainless steel. The canals for filling each half of the cell are drilled in the block following a design indicated by Sirianni *et al.*¹⁰ but arrangements for closing them have been excluded as they are unnecessary (*cf.* Gilbert *et al.*¹¹). One canal from each half of the cell is connected by a stainless steel cannula to the manometer M and the other two are provided with cannulas bent in the shape of spirals ending with short glass capillaries which are connected through standard tapers to the bottoms of 50 ml round flasks. The design is very practical for many reasons. When the filled cell is already free of air bubbles, and in use, the excess of solvent is easily removed to such an extent that the menisci are to be found in the capillaries. When a solution or fresh solvent is to be brought into the cell the steel spirals are pressed together with the result that the menisci rise into the flasks. In this way the cell can be easily kept free of air bubbles during long periods. The cell is filled initially without the inclusion of air bubbles by rapidly sucking a large amount of liquid through each of its halves. Another important point in this particular case is that a final adjustment of the positions of the

Fig. 4. The complete apparatus.

menisci in M can be very sensitively managed by means of the spirals. These permit the attainment of level differences of up to 50 mm. All joints between the cannulas, the manometer M, and the osmotic cell are tightened by means of nuts and teflon packings. The glass capillaries are cemented on to the metal by means of lead oxide and glycerol. The silver blocks have been made as flat as possible in a grinding machine and as silver is somewhat resilient the strong force which can be applied by means of the steel frame is enough to prevent leakage at the membranes. No problems of leakage have arisen.

The thermostat is filled with water and contains two electric heaters, one of which is continuously in operation while the other is regulated by the contact thermometer and a relay. The stirrer is made as a double pump circulating the water also through the manometer M and the liquid compensator LC. The osmotic cell is completely immersed in a small bath mounted inside the main thermostat. The temperature fluctuations in the inner bath are smaller than $\pm 0.005^\circ$.

Fig. 4 shows the complete apparatus.

As mentioned above the apparatus has been mainly used for dynamic osmometry. In a subsequent paper⁶ the technique and results will be extensively discussed. In this paper a typical result of such measurements will be shown where the method of extrapolation is the one used by Gee¹², Montonna and Jilk¹³ and others (e.g. Refs. 2 and 3). The rate of flow of solvent through

Fig. 5. Typical rate curves for a polystyrene fraction (Ref. 14) in methyl ethyl ketone and the corresponding $\frac{\pi}{c} - c$ relationship.

the membrane, $\frac{dh}{dt}$ at a certain level difference h between the menisci, is determined and plotted against h . A straight line is obtained, the intercept of which on the h -axis gives the value of h where $\frac{dh}{dt} = 0$, i.e. the equilibrium value. Fig. 5 shows the results of some measurements on a polystyrene fraction in methyl ethyl ketone for different concentrations using an Ultracellafilter membrane. From this figure some idea of the sensitivity of the rate determination can be obtained. The accuracy of the extrapolation is generally about 0.01–0.02 mm. The corresponding $\frac{\pi}{c} - c$ plot is drawn in the same figure.

The molecular weight of the fraction, denoted PSF—III, an international polystyrene fraction, has been found to be 540 000. A survey of measurements on this sample can be found in "Report on Molecular Weight Measurements of Standard Polystyrene Samples"¹⁴ (the fraction is labelled III).

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