A Two-Capillary Viscosity Method Monitored by an Analytical Balance

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Synopsis

By the simultaneous use of two capillaries, one for solution and one for solvent, and determination of the weight difference of the effluxing liquids with an analytical balance, it is possible, without time measurement, to determine the relative viscosity of a solution with high accuracy. Nylon capillaries were used in the experiments. The equation necessary for calculation of the relative viscosity is derived. The method is particularly useful for very dilute polymer solutions and for the study of low molecular weight substances and lends itself to study of the corrections common in capillary viscometry. Literature values for glucose were confirmed with the method, but low values were found for sodium chloride. The use of bundles of capillaries makes it possible to study the boundary between solvent and solution and to study the possible migration of polymer molecules, in terms of size, toward or away from the walls under conditions of capillary flow. The method can also be used for studying viscous properties of liquids that vary with time.

INTRODUCTION

The measurement of the relative viscosity or the specific viscosity of a solution by conventional capillary viscometry involves two independent measurements, one of the solution and one of the solvent. In very dilute polymer solutions or with solutes of low molecular weight, great care must be taken to control the temperature. Although the relative viscosity varies much less with temperature than does the absolute viscosity, especially for dilute solutions, to obtain the relative viscosity to six significant figures, for example, requires a temperature constancy of the order of 0.001°C. The use of some kind of difference method where the solution and solvent are studied simultaneously, under equal temperature conditions, would therefore be of benefit. Such a method involves the use of two viscometers at the same time.

Hess[1] measured the difference in efflux volumes from two nearly identical, horizontal capillaries which were exposed to the same pressure drop. The precision obtainable from a volume measurement was insufficient, however, to measure low relative viscosities.

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In this paper a method is presented in which the volume measurements are done by weighing. As a result, the method is apparently capable of much greater accuracy than is obtainable with conventional capillary viscometry. Time measurements of high precision, usually necessary in conventional capillary viscometry, are not required, as time cancels out from the working formula. It will also be seen that the method can be used to study viscous properties that vary with time.

THEORY

Two capillary viscometers are used simultaneously, as can be seen in Figure 1, item 3. They will be assumed to be nearly identical, although the theory does not necessarily require this. A common pressure is applied to both the viscometers (Fig. 1, items 12). The liquids in the reservoirs (items 1 and 2) as well as in the receivers (item 7) are kept at approximately the same level in order to keep the hydrostatic pressure low in comparison to the applied pressure. The capillaries are dipped into the two receivers
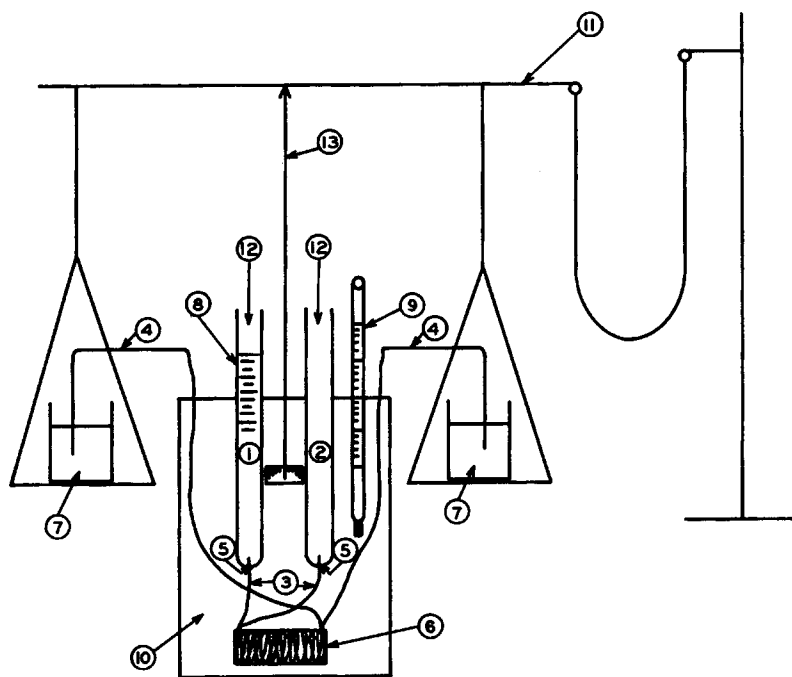
I. 2. RESERVOIRS.   3. CAPILLARIES.   4. COARSE CAPILLARIES.
5. EPOXY SEALS.   6. GLASS CYLINDER ON WHICH CAPILLARIES ARE WOUND.
7. RECEIVERS.   8. VOLUME GRADUATIONS.   9. THERMOMETER.
10. WATER BATH.   II. CHAIN BALANCE.   12. APPLIED PRESSURE.
13. BALANCE POINTER BEHIND BATH.

Fig. 1. Sketch of the two-capillary balance viscometer.

which are placed on the two pans of a balance.   Two experiments (A and B) are performed.

Experiment A.   The solution (viscosity $= \eta$) to be studied is placed in viscometer no. 1 and the solvent (viscosity $= \eta_0$) in viscometer no. 2. According to the Poiseuille law (all corrections are neglected) one obtains

$$\eta = C_1 \cdot P_1 \cdot t_1/V_1 \tag{1}$$

and

$$\eta_0 = C_2 \cdot P_1 \cdot t_1/(V_1 + \Delta V_1) \tag{2}$$

where C_1 and C_2 are viscometer constants, P_1 is the applied pressure, and V_1 and $(V_1 + \Delta V_1)$ are the volumes of liquid flowing through the two capillaries during time t_1.

The change in weight difference between the two receivers, w_1, is

$$w_1 = V_1 \cdot \rho - (V_1 + \Delta V_1) \cdot \rho_0 \tag{3}$$

where ρ and ρ_0 are the densities of the solution and the solvent, both corrected for air buoyancy.   It can be noted that w_1 is often a negative number.

From eqs. (1) to (3) one obtains

$$\eta/\eta_0 = (C_1 \cdot \rho/C_2 \cdot \rho_0) \cdot \left(1 - \frac{w_1}{V_1 \cdot \rho}\right) \tag{4}$$

Experiment B.   In the second experiment the solvent and the solution are interchanged.   In the same way as above one obtains

$$\eta_0/\eta = (C_1 \cdot \rho_0/C_2 \cdot \rho) \cdot \left(1 - \frac{w_2}{V_2 \cdot \rho_0}\right) \tag{5}$$

where w_2 is the change in weight difference between the two receivers while the volume V_2 is flowing through capillary no. 1.

By combining eqs. (4) and (5) one obtains the final formula

$$\eta/\eta_0 = (\rho/\rho_0) \cdot \sqrt{\frac{1 - w_1/V_1 \cdot \rho}{1 - w_2/V_2 \cdot \rho_0}} . \tag{6}$$

From eq. (6) one can estimate how the error in the relative viscosity depends upon the accuracy in the measurements.   The ratio ρ/ρ_0 can be determined with an accuracy of 10^{-5} to 10^{-6} without great difficulty.   This means that if the capillaries are well matched and the viscosities of the solution and the solvent are close, the weight-to-volume ratio in eq. (6) must be determined with about the same accuracy as the density ratio in order to keep the error in the relative viscosity at the same level.   If V is chosen as 10 ml and ρ is put equal to 1 the weight difference w must be determined with an accuracy of 0.1 to 0.01 mg to obtain the relative viscosity with five or six significant figures, well within the capacity of modern weighing techniques.   The V value must be determined with the

same number of significant figures as are expected in the specific viscosity
$[(\eta/\eta_0) - 1]$.

EXPERIMENTAL

Preliminary experiments were performed in order to test the applicability
of the above method. The reservoirs of the viscometers were constructed
of glass tubes with a diameter of about 12 mm reduced to a narrow opening
at one end. Nylon capillaries about 1 m long and with an inner diameter
of about 0.12 mm were threaded about 1 cm into the narrow reservoir
openings and sealed in place with epoxy adhesive. Two such tubes with
capillaries, having approximately the same flow characteristics for water,
were placed close to each other and the nylon capillaries were wound paral-
lel, and as close to each other as possible, around a glass tube 2 cm long and
15 mm wide. In order to minimize the hydrodynamic pressure drop in the
parts exposed to temperature fluctuations, the free ends of the capillaries
were extended with two short pieces of nylon capillary of somewhat greater
dimension ($\sim$0.4 mm). This precaution may be unnecessary when better
temperature control is attained. Epoxy adhesive was again used to seal
the extensions to the capillary ends.

The two glass reservoirs extend into a small water bath (item 10) that
holds the glass cylinder (item 6) around which the capillaries are wrapped.
The ends of the capillary extensions emerge from the bath and dip into two
receivers (item 7), one on each of the two pans of an ordinary chain-type
analytical balance of 0.1-mg accuracy. The whole apparatus is enclosed
by the usual balance case. The experiments were carried out in a room
with temperature constancy of about 1°C.

The viscometer reservoirs were filled with a syringe to the same level
as the solution and solvent in the receivers on the balance pans. After
immersing the capillary ends into the beakers the capillaries were freed of
air bubbles by alternate pressure and suction.

The reservoirs were connected to a common compressed air supply of
about 1 atm. The pointer of the balance was kept at the zero point by
continuously adjusting the chain of the balance. Weight readings were
made after even volume intervals marked on reservoir No. 1. A stop
watch was also used to check that the rate of flow was unchanged during the
course of the experiment.

Anhydrous d-glucose (5 g/l.) in water was used as the test solution. The
change in weight difference was measured for every 1.0 ml of fluid flowing
through capillary no. 1. Additional measurements with solvent in both
viscometers and with solution in both viscometers were performed and eq.
(4) was applied as a comparative control. The results are seen in Table I,
from which the relative viscosity of the solution can be calculated using
eq. (6). Density ratios were obtained from the literature.[2] The result
can be seen in Table II, where the relative viscosity of other aqueous solu-
tions are also given.

TABLE I

Data from Measurements with 5.00 g/l. Glucose in Water[a]

| Viscometer liquids | | w, mg | V, ml | Temperature range, °C |
viscometer no. 1	viscometer no. 2			
Glucose (5 g/l.)	Water	54 ± 2	1.00	22.1–22.3
Water	Glucose (5 g/l.)	72 ± 2	1.00	22.2–22.4
Water	Water	65 ± 1	1.00	21.7–22.0
Glucose (5 g/l.)	Glucose (5 g/l.)	60 ± 2	1.00	22.1–22.2

[a] $\rho/\rho_0 = 1.0021$ (from *International Critical Tables*[2]).

TABLE II

Relative Viscosities of Aqueous Glucose and Sodium Chloride Solutions[a]

| Solute | Concn., g/l. | η_{rel} | |
		This work	Literature (Ref.)
Glucose	5.00	1.012 ± 0.001	1.013[b] (3)
Glucose	10.00	1.026 ± 0.001	1.026[b] (3)
NaCl	5.72	0.994 ± 0.003	1.009 (4)
NaCl	57.20	1.080 ± 0.003	1.090 (4)

[a] For temperature see Table I.

[b] Calculated from Figure 1 in Ihnat and Goring.[3]

For the glucose solutions the agreement with the literature data must be regarded as satisfactory, but for the sodium chloride solutions the difference between the experimental and literature values is far beyond the experimental error. As a check, the same solutions of glucose and sodium chloride were run in Cannon-Ubbelohde viscometers and good agreement was found with the literature values.

The suspicion that osmotic effects were responsible was ruled out when no effect was found upon replacing the water in the bath with a higher concentration of sodium chloride than was measured inside the capillaries. The reason for low values with sodium chloride is not known, although interaction with the nylon capillaries or the effects of the applied pressure may be responsible.

DISCUSSION

The accuracy of the experiments can be easily increased by using an automatic balance of modern type and by improved temperature control. The latter is indeed necessary in order to obtain the high precision inherent in the method. Because of the close proximity of the two capillaries, however, control to better than 0.01 °C is not needed to obtain the highest precision.

Viscometer corrections were neglected in the present study, but the experiments were performed in such a way and at such viscosity levels that the corrections can be expected to be very small. On the other hand, equip-

ment of this type is well adapted for the study of such corrections. A special problem occurs because the capillaries are not straight. This has, however, recently been treated by Schurz and Tomiska[5] and does not seem to be serious.

The good reproducibility of the experiments indicates that the mechanical stability of the thin-walled nylon capillaries were good. The use of other capillaries than nylon in the apparatus offers new possibilities for the study of capillary flow. By using a bundle of such capillaries sealed at each end so that flow is confined within the capillaries, the change in the boundary between a solvent and solution can be studied while flow occurs. Deviations from Newtonian flow laws can be detected by observing the concentration-versus-elution volume curve from such a capillary bundle, by observing the movement of the dissolved molecules toward or away from the wall of the capillary during flow.

The capillaries used in this work have an inner diameter lower than is generally recommended for viscosity determinations. Further work with other diameters is planned when these become available.

Limitations of the Method

Some limitations of the present method must be mentioned. The sensitivity s(radians per unit weight) of the balance decreases when the ends of the capillaries are dipped into the receivers on the pans of the balance. It can be shown that

$$1/s = (1/s_0) + 2 \cdot \pi \cdot \rho \cdot l \cdot r^2 \tag{7}$$

where s_0 is the sensitivity of the balance without capillaries dipping into the receivers, ρ is the density of the liquids in the receivers (assumed to be the same), l is the length of the balance arm, and r is the outer radius of the capillaries. This effect was quite noticeable though not critical with the equipment used in this work. This, of course, puts restrictions upon the size of the capillaries and the balance to be used.

The surface tension forces at the points where the capillary ends dip into the receivers also play an important role. Different readings can be noticed if the equilibrium of the balance is approached from a weight value too high or too low. This difficulty can be overcome by approaching the equilibrium from only one direction or by adding a surface-active agent to the liquids in the receivers. Both these methods were used. The same results were obtained in both cases, but the accuracy seemed to be a little higher when surface-active agents were used. It is, however, believed that an automatic balance where the movements of the pans are negligible will eliminate this problem.

The evaporation of the liquids from the receivers must of course be eliminated by proper design of the receivers and their surroundings. In the present work the effect of the evaporation could be neglected.

Study of Viscosity Change with Time

Finally, the possibility of using the apparatus for studying liquids whose viscosities vary with time is proposed. Two experiments are performed. In the first experiment, a standard liquid of constant viscosity η_0 and of density ρ_0 is used in viscometer no. 1 (i.e., the viscometer where the volume readings are made), and the liquid with the varying viscosity η_t and of density ρ (assumed to be constant) is used in viscometer no. 2. The following equation can be derived:

$$\eta_t/\eta_0 = [C_2 \cdot (\rho/C_1) \cdot \rho_0]/\left(1 - \frac{1}{\rho} \cdot \frac{dw_1}{dV_1}\right). \tag{8}$$

Simultaneously dV_1/dt (= a constant) is measured with a stopwatch.

In the second experiment the standard liquid is used in both the viscometers. Then

$$C_2/C_1 = 1 - \frac{w_2}{\rho_0 \cdot V_2} \tag{9}$$

and from eqs. (8) and (9) one obtains

$$\eta_t/\eta_0 = (\rho/\rho_0) \cdot \left(1 - \frac{w_2}{\rho_0 \cdot V_2}\right)\Big/\left(1 - \frac{1}{\rho} \cdot \frac{dw_1}{dV_1}\right). \tag{10}$$

In order to obtain η_t, one first obtains dw_1/dV_1 from the w_1-versus-V_1 curve and then calculates η_t from eq. (10). From the known dV_1/dt value the corresponding value of t can be calculated. This method thus makes it possible to calculate the viscosity of the solution at any time. With conventional capillary viscometry, only an average value covering the time of flow is possible.

References

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