The Differential Viscometer. I. A New Approach to the Measurement of Specific Viscosities of Polymer Solutions

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Synopsis

A new type of solution viscometer is described that measures the specific viscosity directly. This is accomplished with a balanced network of four capillaries arranged in a manner analogous to a Wheatstone bridge. A differential pressure transducer measures the increase in pressure across the bridge when a solution is injected into one of the capillaries while solvent flows continuously in the other three capillaries. The differential pressure is proportional to the specific viscosity of the solution. The differential viscometer is about 10 times more sensitive than a conventional glass tube viscometer, permitting precise measurements of specific viscosities of 0.01 or less. The measurements are also inherently fast, averaging about 3 min per sample. Precision is about 1% RSD. Accuracy was investigated by running standard solutions of sucrose in water, polystyrenes in toluene, and polyethylenes in decalin. The agreement was within 2–3% of the standard values in most cases.

INTRODUCTION

Measurement of relative viscosities of solutions is one of the oldest methods of polymer characterization. Viscosity data can yield valuable information about polymer structure, such as molecular weight, degree of branching, chain stiffness and chain configuration, and the nature of polymer–solvent interactions.[1] In spite of its great utility, in recent years the solution viscosity method has declined in popularity relative to other polymer characterization methods. The reason for the decline is apparent—viscometric methods have not kept pace with the rapid evolution of most analytical methods toward sophisticated instrumentation capable of greater sensitivity, speed, and ease of operations. The glass capillary tubes of Ubbelohde or Cannon and Fenske are still the most widely used viscometers for solution viscosity measurements today. Refinements have been added, such as using light sensors to measure the fall time, or even fully automated systems that flush and load the viscometer tube, measure fall times, compute results, etc. These refinements are helpful in reducing the labor and tedium of manual measurements but do not address the other basic analytical parameters of speed and sensitivity.

For the glass capillary viscometer, the speed and sensitivity of solution viscosity measurements are linked intimately to the precision with which viscosities can be measured. For polymer solutions the usual quantity of

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interest is the intrinsic viscosity [η], also called the limiting viscosity number:

$$[\eta] = \left.\frac{\eta_{sp}}{C}\right|_{c \to 0} \tag{1}$$

Here C is the concentration of the solution, η_{sp} is the measured specific viscosity, and η_{sp}/C is the viscosity number:

$$\eta_{sp} = (\eta - \eta_0)/\eta_0 \tag{2}$$

where η = the viscosity of solution and η_0 = the viscosity of solvent. In order to measure a specific viscosity of 0.1 with a precision of 1%, the viscosities of solvent and solution must each be measured with a precision of better than 0.1%. This is about the average precision of the typical glass capillary viscometer system with fall times in the range of 100–200 ss. In order to increase the precision and thence the sensitivity, fall times must be increased proportionately. Priel[2] has explored the ultimate precision of glass capillary viscometry. Using fall times of about 1000 s, special apparatus for determining the meniscus, extremely tight control of bath temperature, and stringent cleaning procedures, he was able to obtain precision in viscosity measurements of one part in 5×10^6. It is extremely doubtful that such precision could be approached in routine laboratory use. A routine precision of slightly better than 0.1% appears to be a practical limit.

An important consequence of this limited precision/sensitivity is that extrapolation methods are generally necessary in order to determine the intrinsic viscosity. This multiplies the analysis time in proportion to the number of dilutions run, usually 4–6. If greater sensitivity could be obtained so that specific viscosities in the vicinity of 0.01 could be determined directly, the extrapolation procedure would be unnecessary, and much time would be saved in determination of intrinsic viscosities.

In seeking higher sensitivity, it is noted that specific viscosity is the variable to be determined, not the actual viscosities of solvent and solution. Thus, a differential method would be expected to be more sensitive. Blair[3] constructed a capillary viscometer capable of measuring the difference in viscosity between a solvent and polymer solution. Solvent and solution were pumped simultaneously at equal flow rates through separate capillaries having equal flow resistances. The differential pressure required to pump the solvent and solution at equal flow rates is proportional to the specific viscosity. Although it is conceptually sound, the Blair device apparently lacked the operational refinements necessary to make it a practical viscometer. The differential viscometer (DV) of Haney[4–6] also utilizes differential pressure measurement on separate capillary flowstreams of solvent and solution. However, the concept is distinct from Blair's in that the flow rates are not equal. Instead, the solution capillary is one leg of a four-capillary bridge analogous to a Wheatstone Bridge. It will be shown below that this principle of differential measurement when combined with suitable pumping and injection apparatus yields a solution viscometer of un-

matched sensitivity, speed, and operational ease. With slight modification the DV can also be used as an on-line viscosity detector for size exclusion chromatography, a subject that is dealt with in a companion paper.[7]

INSTRUMENTATION

Principles

A simplified schematic of the DV is shown in Figure 1. Solvent at constant inlet pressure P_i flows continuously through the bridge network, which consists of four capillaries R_1–R_4 of equal flow resistance. Two sample reservoirs A and B can be switched simultaneously in or out of the flow streams by means of tandem switching valves S_A–S_B. When the reservoirs are out of the streams (BYPASS position of S_A–S_B), they can be filled with solutions by means of a sample introduction system not shown. Typically, reservoir A is filled with the sample solution and reservoir B is filled (or remains filled) with solvent. In the BYPASS position solvent is flowing through all four capillaries, producing equal flow resistances and yielding a zero or baseline reading on the differential pressure transducer (Fig. 2).

Now when the valves S_A–S_B are turned to the INJECT position the sample solution in reservoir A flows through capillary R_3, but solvent flows through the other three capillaries R_1, R_2, R_4. If the sample solution is more viscous than the solvent, there will be a pressure increase on the left side of the bridge. When the solvent is completely purged from R_3 by the solution the differential pressure attains a steady state value ΔP above the baseline value. Eventually, solvent breaks through reservoir A and the differential pressure will gradually return toward base line. At this point the measurement is completed, so the values S_A–S_B are switched back to BYPASS for loading with new sample. Solvent quickly purges the old solution from R_3, and the differential pressure resumes the baseline.

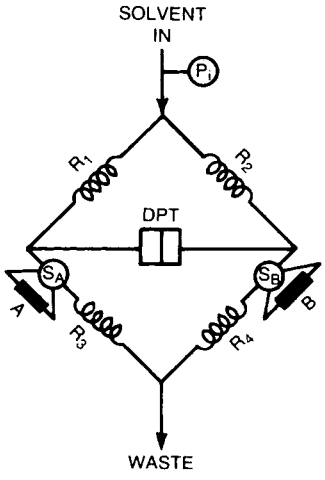

Fig. 1. Simplified schematic of differential viscometer.

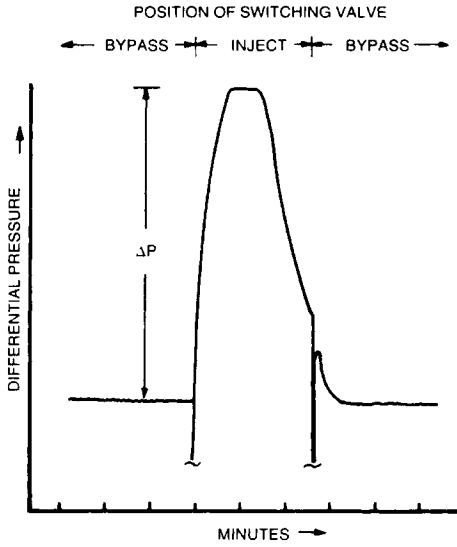

Fig. 2. Injection of sample solution: Sample, polystyrene standard 100,000 MW; solvent, tuluene; concentration, 0.19 mg/mL; flow rate, 3 mL/min; P_i, 41 KPa; temperature, ambient.

Calculation of Specific Viscosity

The measured quantities are bridge inlet pressure P_i, measured with respect to the outlet, and the differential pressure at steady state ΔP:

$$\frac{\Delta P}{P_i} = \frac{P_1 - P_2}{P_i} \tag{3}$$

where P_1 is the pressure drop across R_3 and P_2 is the pressure drop across R_4. Since solvent is flowing through equal flow resistances R_2 and R_4 at the same flow rate, $P_1 = 2P_2$:

$$\frac{\Delta P}{P_i} = \frac{1}{2}\left(\frac{P_1}{P_2} - 1\right) \tag{4}$$

Applying Poiseuille's law to R_3 and R_4, we have

$$\frac{P_1}{P_2} = \frac{\eta Q_1}{\eta_0 Q_2} \tag{5}$$

where Q_1 is the flow rate through R_1, R_3, Q_2 is the flow rate through R_2, R_4, η is the viscosity of the solution and η_0 is the viscosity of the solvent. The ratio of flow rates Q_1/Q_2 is equal to the inverse ratio of the total resistance in each side of the bridge:

$$\frac{Q_1}{Q_2} = \frac{\eta_0 + \eta_0}{\eta_0 + \eta} = \frac{2\eta_0}{\eta_0 + \eta} \tag{6}$$

Combining Eqs. (4)–(6) yields

$$\frac{\Delta P}{P_i} = \frac{1}{2}\left(\frac{\eta - \eta_0}{\eta + \eta_0}\right) \tag{7}$$

Inserting the definition of specific viscosity in eq. (7) yields

$$\frac{\Delta P}{P_i} = \frac{\eta_{sp}}{2\eta_{sp} + 4} \tag{8}$$

which may be rearranged to

$$\eta_{sp} = \frac{4\Delta P}{P_i - 2\Delta P} \tag{9}$$

Equations (8) and (9) are exact equations subject to the following assumptions:

(a) The capillaries have equal flow resistances. This condition can be obtained by trial and error to any desired degree of accuracy.

(b) The flow through the capillaries is in accord with Poiseuille's law. This law will hold for low flow rates in capillaries of high length/diameter ratios. The flow rates and capillary dimensions can be chosen to meet this requirement.

In the situation where two different solutions of viscosities η_1 and η_2 are injected simultaneously from reservoirs A and B, respectively, a similar analysis leads to

$$\frac{\Delta P}{P_i} = \frac{\eta_0(\eta_1 - \eta_2)}{(\eta_1 + \eta_0)(\eta_2 + \eta_0)} \tag{10}$$

This can also be expressed in terms of the specific viscosities.

$$\frac{\Delta P}{P_i} = \frac{\eta_{sp}(1) - \eta_{sp}(2)}{[\eta_{sp}(1) + 2]\,[\eta_{sp}(2) + 2]} \tag{11}$$

If the specific viscosity of one solution is known, e.g., a reference sample, eq. (11) can be used to derive the specific viscosity of the other solution.

Design and Construction

A plumbing schematic of the DV is shown in Figure 3. The capillary bridge R_1–R_4, tandem switching valves, and sample reservoirs are contained within a heated valve compartment capable of maintaining constant, evenly distributed temperature in the range from ambient to 150°C.

Valve Compartment

This consists of a heated inner chamber separated by insulation from an outer chamber. The inner chamber is an aluminum cylinder of dimensions

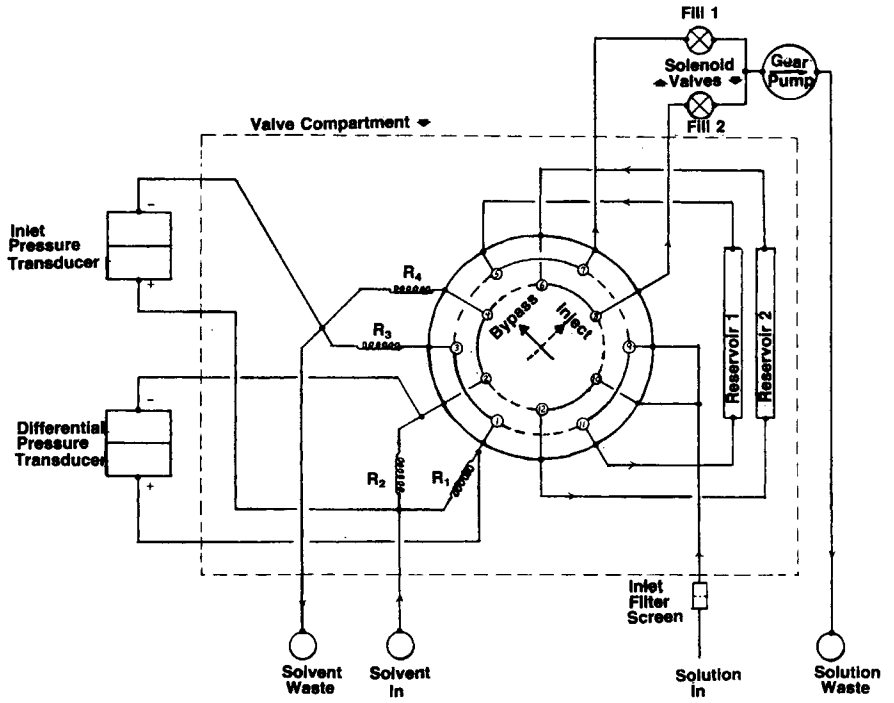

Fig. 3. Plumbing schematic of differential viscometer.

6 in. OD × 3 in. L × 0.25 in. TH, with each end of the cylinder capped with 0.1875 in. thick aluminum plates. A silicone mat heater is wrapped tightly around the outside of the cylinder, and probes for temperature control and readout are also attached to the outside cylinder wall. One inch of fiberglass insulation surrounds the inner chamber. The outer chamber is also cylindrically shaped and fabricated of 0.03 in. stainless steel sheet. The valve itself is mounted along the cylindrical axis with the valve handle protruding through the compartment and out the front panel of the instrument.

Valve

The tandem switching valves of Figure 1 are actually on a single 12-port, two position switching valve obtained from Valco instruments, Houston, Texas. The valve has two independent tiers of six ports each as shown in Figure 3. Alternate adjacent pairs of ports are connected together in the BYPASS and INJECT positions. The valve body is constructed of stainless steel and the rotating shaft seal is a filled PTFE compound. Maximum operating temperature is 175°C and maximum pressure is 400 psig.

Capillaries

The capillaries can be made of various material (glass, PFTE, stainless steel) and over a limited range of dimensions, depending upon the demands of the application. The work described herein was obtained with stainless steel capillaries of 0.625 in. OD with either 0.02 in. ID × 8 ft L or 0.016

in. ID × 3 ft L. In either case the capillaries have a sufficiently high length/internal diameter ratio that kinetic energy corrections and end effects should be negligible.

Reservoirs

These are constructed of a size and material to be consistent with the capillaries. For the 0.0625 in. OD × 0.016 in. ID × 3 ft L SS capillaries, the reservoirs were made of 0.125 in. OD × 0.105 in. ID × 9 in. L SS tubing. This provides a reservoir volume of 1.27 mL, which is adequate to thoroughly purge the capillry volume of 0.12 mL. In general, this ratio of reservoir volume to capillary volume must be maintained because flow through the reservoirs is not generally plug flow but laminar flow, so that only about half the reservoir volume is available as pure solution.

Sample Loading System

A single inlet tube (0.125 in. OD PTFE) with a 100-mesh filter screen in-line is dipped into the sample solution. A pushbutton switch activates the small gear pump and opens one of the solenoid valves to flush the selected reservoir with sample solution. Sample flush volume must be sufficient to purge out all old sample/solvent, typically about 6–8 mL.

Solvent Delivery System

Solvent is fed to the inlet of the capillary bridge at constant pressure by means of a pressurized solvent tank. A schematic of the solvent controller containing this tank is shown in Figure 4. Solvent is admitted to the tank by vacuum suction. The solvent is then degassed under vacuum with stirring. The tank is then pressurized with helium and controlled at the desired level with a pressure regulator. The solvent is filtered in-line on the way to the capillary bridge.

Pressure Transducers

Both the inlet pressure and the differential pressure are measured with differential pressure transducers of the magnetic reluctance type (Validyne Engineering, Northridge, CA). The pressure cavities of the transducers and the connecting tubing (0.03 in. ID PTFE) must be filled with liquid. This is accomplished by bleeding the solvent through the pressure cavities by means of bleed screws mounted in the side walls of the transducers. The inlet transducer has a range of 0–100 kPa, and the differential transducer has a range of 0–5 kPa. Precision of measurement on both transducers is 0.5% including linearity and hysteresis.

The differential transducers are calibrated externally with a dual liquid column manometer constructed of two glass tubes mounted side-by-side in a vertical position. The botton end of each tube is connected to one of the pressure cavities, and the tubes are filled with a liquid of known density to a measured height differential. Calibrations have been found to be constant over a period of several months of use. The same manometer and calibrating liquid is used for both transducers so that systematic errors will tend to cancel in the ratio.

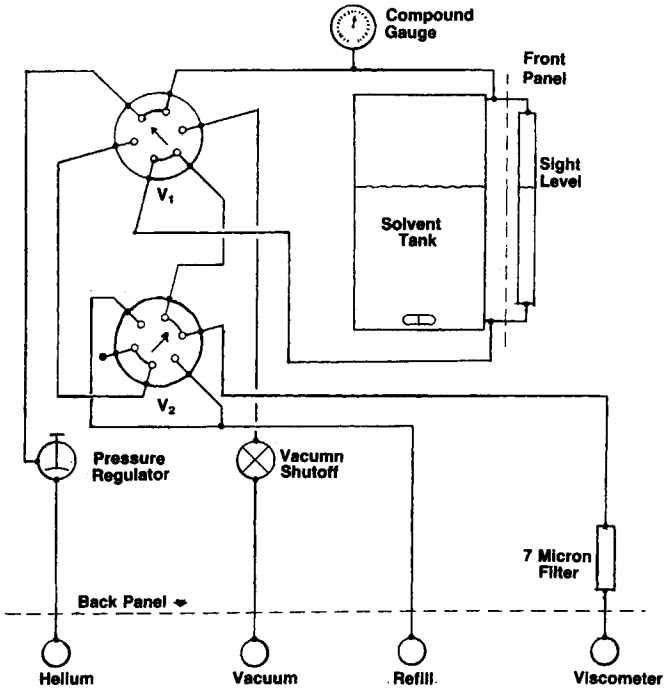

Fig. 4. Plumbing schematic of solvent controller.

RESULTS AND DISCUSSION

The basic performance of the instrument was evaluated with THF as solvent and a 10% H_2O/THF test solution. The differential pressure ΔP was measured as a function of inlet pressure P_i with this solution in reservoir A. These data are shown in Table IA and plotted in Figure 5. The

TABLE I
Differential Pressure vs. Inlet Pressure[a]

A. Sample in Reservoir A, Flow in Normal Direction through the Bridge

P_i (kPa)	ΔP (Pa)	η_{sp}
9.2	760	0.396
12.7	1048	0.395
16.1	1320	0.392
19.7	1615	0.392
23.7	1930	0.389
27.2	2225	0.391
31.7	2600	0.392
36.9	3000	0.388

B. Alternate Reservoirs and Directions of flow

Reservoir	Flow direction	P_i (KPa)	ΔP (Pa)	η_{sp}
A	Normal	19.7	1615	0.392
B	Normal	19.6	1620	0.396
A	Reverse	19.2	1610	0.403
B	Reverse	19.2	1600	0.400

[a] Solvent, THF; sample, 10% H_2O/THF; temp, ambient.

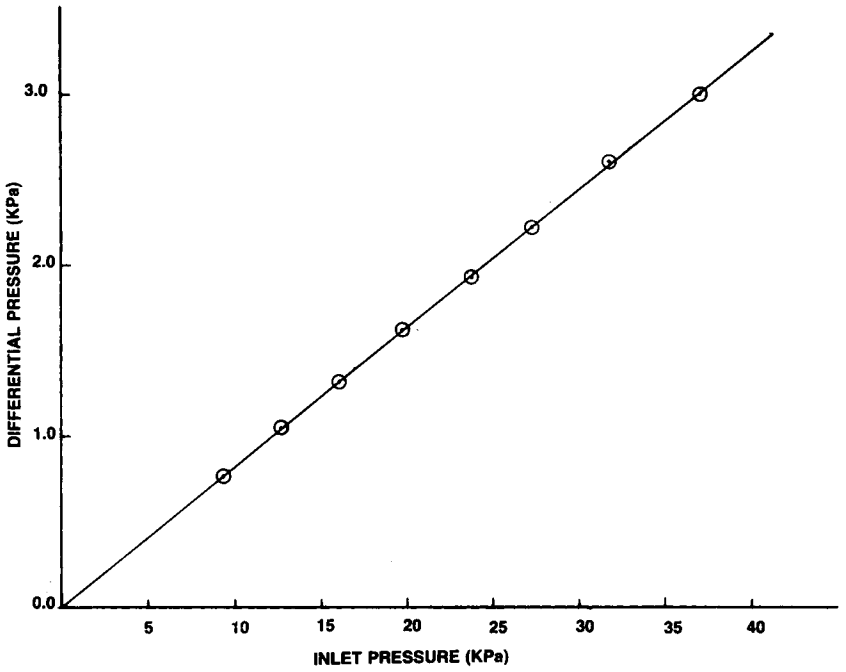

Fig. 5. Plot of data in Table I (a).

ΔP is seen to be exactly proportional to P_i as predicted by eq. (8). Table IB shows data obtained using each reservoir with the normal direction of solvent flow and then with the direction of flow reversed. The good agreement of this data shows that the flow resistance of the four capillaries are very nearly equal and that the flow resistance of the valves, reservoirs, and connecting lines are small with respect to that of the capillaries. Absorption of air in the solvent can produce degassing effects, particularly with THF. Figure 6 shows three blank THF injections at high sensitivity. With a vacuum degassed sample of THF, the blank is negligible. With an air saturated sample of THF, a small negative blank is observed, indicating the air absorption decreases the THF viscosity. If the THF sample is pumped

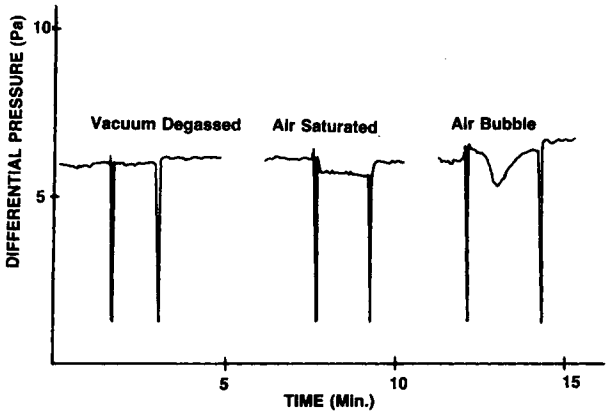

Fig. 6. Effect of air absorption in THF solvent blank injections.

at high flow rates through the sample reservoir, it may degas *in situ*, forming bubbles and producing a large excursion of ΔP. With THF it was found best to work with degassed solvent in order to avoid the bubble formation. The other solvents investigated, including water, did not form bubbles as much as THF. Accuracy was investigated by determinations of three set of standards.

Sucrose

Specific viscosity measurements were made on aqueous sucrose solutions in the concentration range of 1–10 wt %. This data is shown in Table II along with the reference values. The agreement is excellent in spite of the fact that the current data was obtained at 25°C rather than 20°C as was the reference data. Actually, a few degrees temperature change seldom makes an appreciable difference in specific viscosities. It is the solvent viscosity that is most sensitive to temperature.

Polystyrene

Ten narrow distribution molecular weight standards were run in toluene solvent at 25°C. The concentrations were made so that specific viscosities would fall in the range of 0.02 or less. At this range of specific viscosity, the viscosity number η_{sp}/C is very close to the intrinsic viscosity. The data are shown in Table III along with independent measurements of the intrinsic viscosities of five of the samples by the conventional Ubbelohde method. The agreement between the two methods is good except for the 233,000 and the 1,800,000 standards. A Mark–Houwink plot of the differential viscometer data is shown in Figure 7. From the linear fit to the Mark–Houwink equation, the best value of η_{sp}/C for the 233,000 standard is 0.812, which is close to that found by DV of 0.830. However, for the 1,800,000 standard the best value calculates to be 3.64, which is closer to the Ubbelohde value of 3.54 than to the DV value of 4.00.

Polyethylene

NBS polyethylene standards 1475 and 1476 were run in decalin at 135°C. The data are shown in Table IV. Two concentrations differing by a factor

TABLE II
Viscosity of Standard Sucrose Solutions[a]

Concn (wt %)	P_i (kPa)	ΔP (Pa)	η_{sp} [Eq. (9)]	η_{sp} (Ref. 8)
1.00	33.1	213	0.0260	0.026
2.00	33.1	434	0.0539	0.053
3.00	32.9	657	0.0832	0.082
4.00	32.9	870	0.112	0.112
5.00	32.9	1119	0.146	0.144
6.00	32.8	1345	0.179	0.177
7.00	32.8	1576	0.213	0.213
8.00	32.7	1813	0.249	0.251
9.00	32.6	2065	0.290	0.291
10.00	32.3	2288	0.330	0.333

[a] Solvent, water; temperature, ambient (25°C).

TABLE III
Intrinsic Viscosities of Polystyrene Standards[a]

Mol wt	Concn (g/dL)	ΔP (Pa)	η_{sp}	η_{sp}/C	$[\eta]^b$
9,000	0.2374	163	0.0187	0.0789	
17,500	0.1436	152	0.0174	0.121	
50,000	0.0619	136	0.0156	0.252	
100,000	0.0376	132	0.0151	0.402	0.395
233,000	0.0234	169	0.0194	0.830	0.906
390,000	0.0156	155	0.0178	1.14	1.17
600,000	0.0125	184	0.0212	1.69	1.69
900,000	0.0110	199	0.0228	2.07	
1,800,000	0.0050	174	0.0200	4.00	3.54
4,100,000	0.0036	203	0.0233	6.47	

[a] Solvent, toluene; temp, ambient (25°C); P_b 35.1 kPa. Pressure Chemical Co., Pittsburgh, PA.

[b] Obtained by Ubbelohde viscometry, this work.

of 10 were run for each standard. For the low concentrations, the viscosity numbers are approximately equal to the intrinsic viscosities. The precision at high temperature appears to be slightly poorer than near ambient.

The speed of analysis is illustrated in Figure 8, which show five injections in a period of 12 minutes. The speed depends on flow rate, which can be varied with the solvent inlet pressure control so that any solvent with viscosity less than 2 or 3 cP can yield flow rates of about 1–2 mL/min. In this flow rate range and with capillaries 3–5 ft long, the analysis time is in the range of 2–4 min per injection.

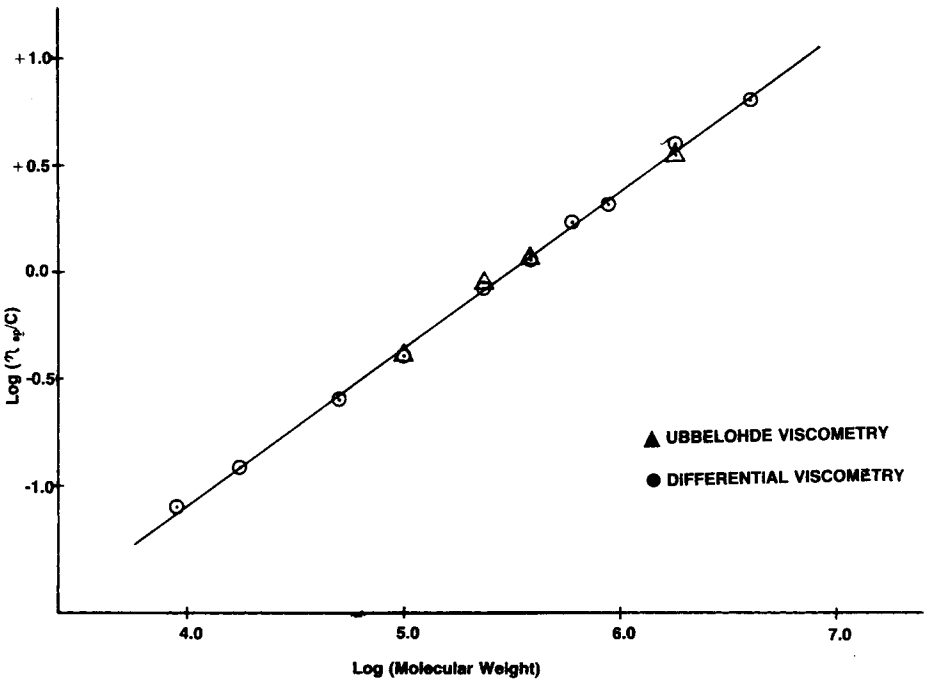

Fig. 7. Mark–Houwink plot for data of Table III. By least squares analysis: $a = 0.734$, log $K = -4.03$ (△) Ubbelohde viscometry; (⊙) differential viscometry.

TABLE IV
Intrinsic Viscosities of Polyethylene Standards[a]

Sample	Concn (g/dL)	η_{sp}	η_{sp}/C	$[\eta]^b$	$[\eta]^c$
NBS 1476	0.1522	0.1727	1.128	1.06	1.04
		0.1742	1.145	1.08	
		0.1712	1.125	1.06	
	0.0149	0.0160	1.074	1.07	
		0.0154	1.034	1.03	
		0.0159	1.067	1.06	
NBS 1475	0.1909	0.2441	1.279	1.17	1.18
		0.2479	1.299	1.19	
		0.2456	1.287	1.18	
	0.0187	0.0226	1.209	1.20	
		0.0226	1.209	1.20	
		0.0228	1.219	1.21	

[a] Solvent, decalin; temperature, 135°C.
[b] Estimated from Huggins equation with $k = 0.4$.
[c] National Bureau of Standards certified values at 130°C.

A unique feature of the DV is that solvent does not have to be the reference. In the dual sample mode of operation each reservoir contains separate solutions, e.g., a control vs. an unknown. This is illustrated in Figure 9, which is a simultaneous injection of two polystyrene standards of identical concentration in toluene but slightly different molecular weight. Solution A consists of 0.551 g/dL of PS standard 600,000 molecular weight. Its specific viscosity was determined in the usual manner as 0.0984, referenced to

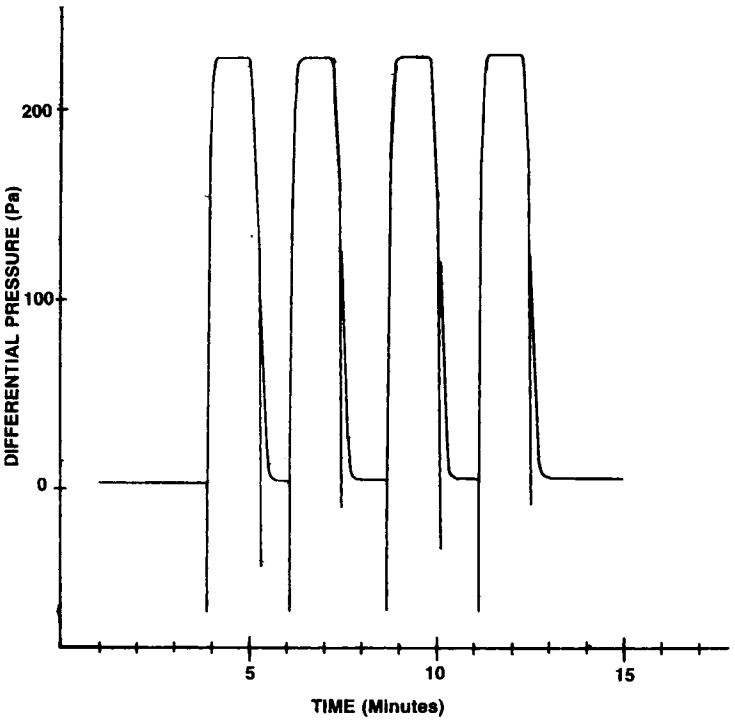

Fig. 8. Repeat injections: Sample, novalak phenol–formaldehyde resin; solvent, THF; concentration, 10 mg/mL; P_i, 14.3 KPa; temperature, ambient.

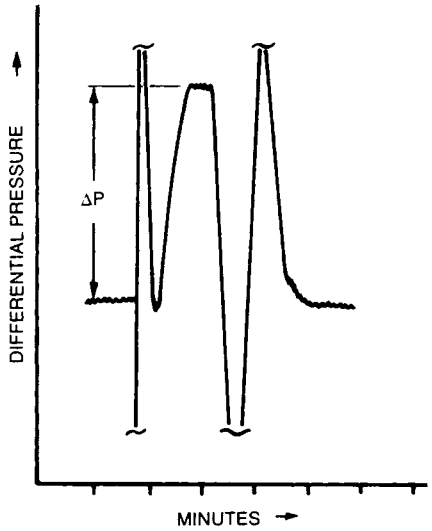

Fig. 9. Dual sample injection.

toluene solvent. Solution B was made by mixing 20 parts of solution A with 1 part of PS standard 390,000 molecular weight, also 0.551 g/dL. The differential pressure shows erratic behavior while the capillaries R_3 and R_4 are partially filled with solutions A and B due to the capillaries not filling at exactly the same rate. However, a distinct plateau is observed, which corresponds to the steady state where both capillaries are completely filled with their respective solutions. Putting the measured ΔP in eq. (11) yields a specific viscosity for solution B of 0.0971. This is precisely the specific viscosity calculated for solution B based on its composition (see Appendix). Thus, the dual sample mode may be used to obtain very high precision in specific viscosity, relative to a reference solution.

CONCLUSIONS

The capillary bridge differential viscometer offers several advantages for viscometry of polymer solutions:

1. Because of the balancing of solvent vs. solution viscosities, high sensitivity and precision is obtained without precise control of temperature. Specific viscosities of 0.01 or less are attainable.
2. Because of the high sensitivity, extrapolation of viscosity numbers to infinite dilution is not necessary.
3. The operation of the instrument is fast and simple. Automation is simplified compared to a glass capillary system.
4. The continuous flow of filtered solvent prevents buildups of polymer or dirt on the capillary walls. Any buildup that does occur is detected and corrected by the baseline.
5. The capillaries have a higher length-to-diameter ratio than ordinary glass capillaires, eliminating kinetic energy and end-effect corrections.

The apparent disadvantages are:

1. It is more complex, and therefore more expensive, than a simple glass capillary setup.

2. The two pressure transducers must maintain calibration in order to get accurate data.

3. With the stainless steel components the present model contains, corrosive solvents, and solutions cannot be used. Fortunately, the majority of polymer solvents do not corrode stainless steel.

The assistance of Dwight R. Hayes, Jr., in all phases of this work is gratefully acknowledged.

APPENDIX

Regarding the data of Figure 9, the specific viscosity of solution B relative to that of solution A may be calculated as follows. It is assumed that the ratio of specific viscosities is equal to the ratio of intrinsic viscosities.

$$\frac{\eta_{sp}(B)}{\eta_{sp}(A)} = \frac{[\eta](B)}{[\eta](A)} \tag{12}$$

This requires that the concentrations of the solutions be the same, which is the case, and also that the dependence of specific viscosity on concentration be the same, which should be a good approximation. Then from the Mark–Houwink equation, it follows that

$$\frac{[\eta](B)}{[\eta](A)} = \left(\frac{\overline{M}_v(B)}{\overline{M}_v(A)}\right)^a \tag{13}$$

where $\overline{M}_v$ is the viscosity-average molecular weight and a is the Mark–Houwink exponent. By definition

$$\overline{M}_v^a = \frac{\sum N_i M_i^{a+1}}{\sum N_i M_i} \tag{14}$$

where N_i is the number of molecules of molecular weight M_i. Using 0.734 as the value of a, $\overline{M}_v(B)$ is calculated from eq. (3) to be 589,488. $\overline{M}_v(A)$ is taken as 600,000. This yields 0.987 for the ratio of specific viscosity of solution B to solution A. The determined value of specific viscosity of solution A was 0.0984, from which the specific viscosity of solution B is calculated to be 0.0971.

References

1. For general treatments see: N. C. Billingham, in *Molar Mass Measurements in Polymer Science*, Wiley, 1977, Chap. 7; P. Onyon, in *Techniques of Polymer Characterization*, P. W. Allen, Ed., Butterworths, London, 1959, Chap. 6.

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