

## A Moderately High Shear Viscometer for Measuring Low Specific Viscosities

F. S. CHAN,\* *Pulp and Paper Research Institute of Canada,  
Pointe Claire, Quebec, Canada*

### Synopsis

A simple, moderately high shear capillary viscometer which can be used up to a shear rate of  $150,000 \text{ sec}^{-1}$  is described. The use of a twin viscometer arrangement has eliminated the need of elaborate pressure control and adjustment units. Experimental results obtained by use of the viscometer to measure the specific viscosities of a charged colloid at two different shear rates are presented.

### INTRODUCTION

During an investigation of the non-Newtonian behavior of a highly charged polystyrene latex,<sup>1,2</sup> viscosity measurements at low concentrations over a wide range of shear were required. For measurement of the low specific viscosities anticipated, it was necessary to use a capillary-type viscometer rather than a rotatory viscometer such as that described by Merrill.<sup>3</sup> The conventional multishear viscometer<sup>4</sup> with different hydrostatic heads is limited to measurement at a maximum shear rate of about  $2,000 \text{ sec}^{-1}$ . Further increase in shear requires driving pressures larger than those provided by the weight of the solution. A mercury-driven high shear viscometer capable of measurements over a wide range of shear rates was described by Maron and co-workers.<sup>5</sup> However, this viscometer suffers from the drawback that mercury comes in contact with the test solution. By applying a combination of positive and negative pressures in a capillary viscometer, Claesson and Lohmander<sup>6</sup> were able to increase the shear rate to  $150,000 \text{ sec}^{-1}$ . But the viscometer required a rather elaborate pressure control and adjustment unit. The present note describes a simple moderately high shear viscometer which is especially effective for the measurement of low specific viscosities in dilute solutions.

### DESCRIPTION AND USE

A schematic diagram of the apparatus is given in Figure 1. One special feature is the use of two identically built viscometers which enable the

\* Present address: Plastics Division, Allied Chemical Corporation, P.O. Box 365, Morristown, New Jersey 07960.

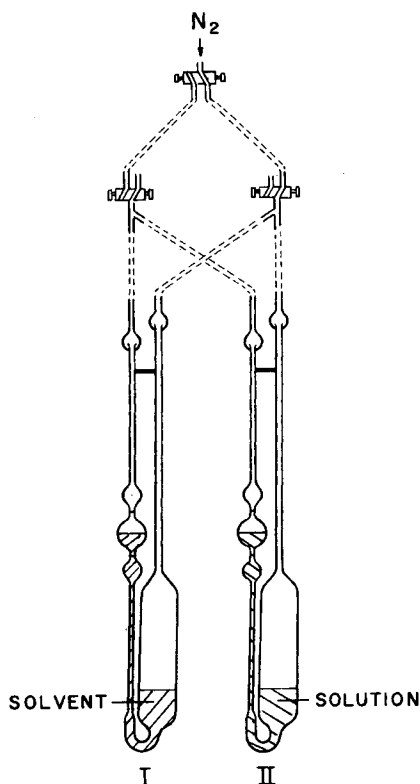


Fig. 1. Schematic diagram of the high shear dual viscometer.

simultaneous measurements of solvent and solution flow times. This arrangement eliminates errors arising from variation of driving pressures in measuring the solvent and solution flow times. Following Claesson and Lohmander,<sup>6</sup> the important dimensions of the viscometers are: bulb volume, 7 ml; capillary length, 10 cm; capillary radius, 0.1 mm.

The openings of the viscometers are connected by ball-and-socket joints and pressure tubing to three three-way stopcocks arranged in the manner shown in Figure 1. By manipulating the stopcocks, the two viscometers can be opened either to a source of compressed nitrogen or to the atmosphere. The applied nitrogen pressure is adjusted by means of a constant-pressure supply valve to  $\pm 0.5$  mm Hg as read from a mercury manometer. Carbon dioxide impurity in the nitrogen is removed by passage through tubes filled with Ascarite and calcium sulfate. Finally, the gas is filtered through a sinter glass filter before being passed into the viscometers.

In each viscometer, the total driving pressure ( $P_t$ ) is the sum of the nitrogen pressure ( $P_n$ ) and the hydrostatic pressure ( $P_h$ ), due to difference in height of the liquid in the viscometer, i.e.,

$$P_t = P_n + P_h.$$

$P_h$  varies with the amount of liquid in the viscometer and may be either

positive or negative, depending on the direction of flow. In the present case,  $P_h$  and thus  $P_t$  may change by as much as 5 mm Hg. This variation is eliminated by measuring the total time taken for the solution to flow down the bulb and then up again by reversing the nitrogen pressure. Thus, the average driving pressure is  $P_h$  and is independent of the amount of liquid present in the viscometer. This method permits the solution to be diluted in situ without altering the average shear rate.

Owing to unavoidable minor differences in the dimensions of the two viscometers, the solvent flow time in viscometer I has to be multiplied by a factor  $A$  before comparison can be made with the solution flow time in viscometer II. The factor  $A$  is close to unit and is the ratio of the solvent flow times in viscometers II and I measured under the same driving pressure:

$$A = \frac{(t'_{\text{up}} + t'_{\text{down}}) \text{ viscometer II}}{(t'_{\text{up}} + t'_{\text{down}}) \text{ viscometer I}} \quad (1)$$

The relative viscosity of a solution is then calculated from

$$\eta_r = \frac{(t''_{\text{up}} + t''_{\text{down}}) \text{ viscometer II}}{(t'_{\text{up}} + t'_{\text{down}}) \text{ viscometer I} \times A} \quad (2)$$

where  $t'$  and  $t''$  refer to the solvent and solution flow times, respectively.

To determine the value of  $A$  in eq. (2), equal volumes of solvent were added to both viscometers which were immersed in a constant-temperature bath through the ball-and-socket joints. After setting a certain nitrogen pressure, the three stopcocks were turned in such a manner that one arm of each viscometer was opened to the nitrogen and the other to the atmosphere. The flow times of the liquid in the two viscometers were measured simultaneously with two stopwatches reading to 0.1 sec. The value of  $A$  was

TABLE I  
Reduced Viscosities and Concentrations of Fraction  $F_1^a$

$I_E = 0.0001M, A = 0.9460$			$I_E = 0.00018M, A = 0.9448$		
$c, \text{g dl}^{-1}$	$\eta_{sp}/c, \text{dl g}^{-1}$		$c, \text{g dl}^{-1}$	$\eta_{sp}/c, \text{dl g}^{-1}$	
	9,000 $\text{sec}^{-1}$	16,000 $\text{sec}^{-1}$		9,000 $\text{sec}^{-1}$	16,000 $\text{sec}^{-1}$
0.323	0.184	0.168	0.566	0.158	0.146
0.249	0.171	0.161	0.435	0.149	0.139
0.180	0.161	0.153	0.314	0.138	0.132
0.115	0.148	0.146	0.202	0.128	0.124
0.075	0.144	0.140	0.132	0.122	0.120
$I_E = 0.0004M, A = 0.9453$			$I_E = 0.001M, A = 0.9473$		
0.696	0.145	0.136	0.761	0.109	0.105
0.535	0.137	0.131	0.585	0.106	0.103
0.387	0.130	0.125	0.423	0.102	0.099
0.249	0.121	0.119	0.272	0.100	0.094
0.162	0.117	0.118	0.177	—	0.098
0.095	—	0.112			

<sup>a</sup> Measured in the high shear viscometer at various ionic strengths and shear rates of 9,000 and 16,000  $\text{sec}^{-1}$  by isoionic dilution.

TABLE II  
Reduced Viscosities and Concentrations of Fraction  $F_3^a$

$I_E = 0.0003M, A = 0.9389$			$I_E = 0.001M, A = 0.9478$		
$c, \text{g dl}^{-1}$	$\eta_{sp}/c, \text{dl g}^{-1}$		$c, \text{g dl}^{-1}$	$\eta_{sp}/c, \text{dl g}^{-1}$	
	9,000 $\text{sec}^{-1}$	16,000 $\text{sec}^{-1}$		9,000 $\text{sec}^{-1}$	16,000 $\text{sec}^{-1}$
0.311	0.244	0.228	0.669	0.174	0.164
0.239	0.218	0.205	0.515	0.165	0.157
0.173	0.201	0.182	0.372	0.153	0.150
0.111	—	0.167			
0.312 <sup>b</sup>	0.239	0.222			
0.130 <sup>b</sup>	0.178	0.171			
$I_E = 0.005M, A = 0.9461$			$I_E = 0.01M, A = 0.9469$		
0.569	0.129	0.126	1.116	0.113	0.110
0.438	0.127	0.124	0.930	0.111	0.108
0.316	—	0.121	0.697	0.109	0.106
0.203	0.120	—	0.531	0.107	0.105
			0.360	0.108	0.110

<sup>a</sup> Measured in the high shear viscometer at various ionic strengths and shear rates of 9,000 and 16,000  $\text{sec}^{-1}$  by isoionic dilution.

<sup>b</sup>  $A = 0.9475$

then calculated from eq. (1) from the average of at least ten runs under two different pressures. Because of small changes in dimensions of the two capillaries, the value of  $A$  was redetermined before each measurement.

Having determined  $A$ , exactly 10 ml each of the solvent and solution were introduced into viscometers I and II, respectively. The same measur-

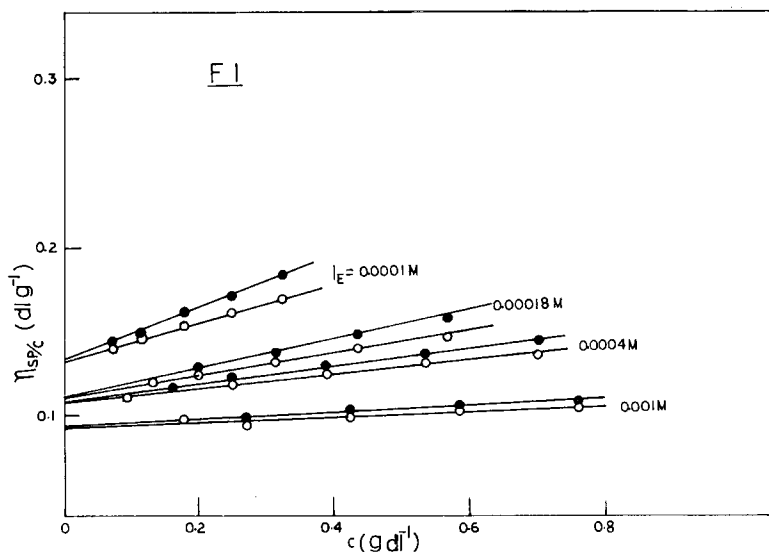


Fig. 2. Reduced viscosity vs. concentration plots of a sulfonated polystyrene latex ( $F_1$ ) measured in the high shear viscometer at different ionic strengths and at average shear rates of (●) 9,000  $\text{sec}^{-1}$  and (○) 16,000  $\text{sec}^{-1}$ .

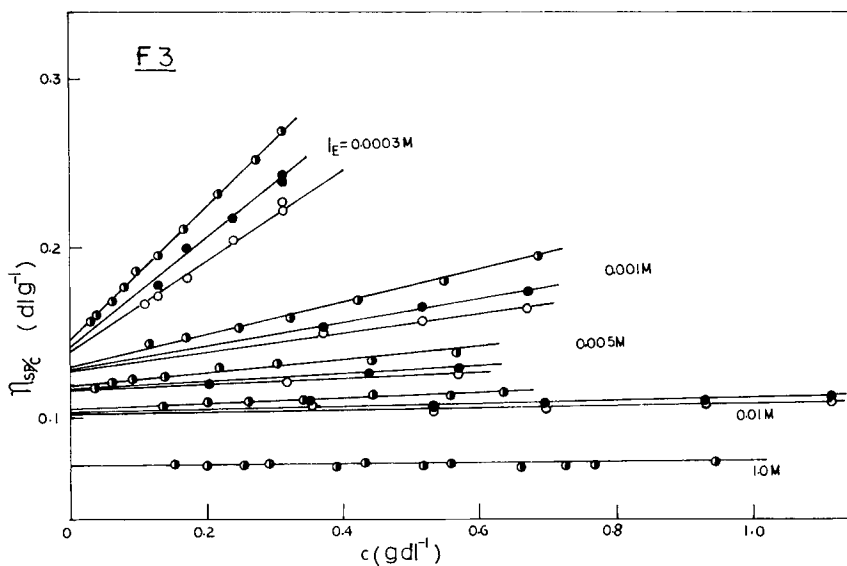


Fig. 3. Reduced viscosity vs. concentration plots of a sulfonated polystyrene latex ( $F_3$ ) measured in the high shear viscometer at different ionic strengths and at average shear rates of (●)  $9,000 \text{ sec}^{-1}$  and (○)  $16,000 \text{ sec}^{-1}$ . Half-filled circles (◐) indicate results obtained in a conventional Ubbelohde viscometer a  $650 \text{ sec}^{-1}$  average shear rate.

ing procedure was repeated at a preset nitrogen driving pressure. The relative viscosity was calculated by means of eq. (2) from the average flow times of three to four runs. Dilutions were performed by adding an equal volume of solvent to the two viscometers.

### EXPERIMENTAL RESULTS

Two fractions of monodisperse sulfonated polystyrene/divinylbenzene latices with a particle radius of  $3.8 \times 10^{-6} \text{ cm}$  and designated  $F_1$  and  $F_3$  as described previously<sup>1,7</sup> were used. Fraction  $F_1$  has a neutralization equivalent of  $0.9 \text{ meq g}^{-1}$ , compared with  $2.7 \text{ meq g}^{-1}$  for  $F_3$ . Measurements were made at  $25 \pm 0.002^\circ\text{C}$  at different ionic strengths by addition of sodium chloride and taking into account the contribution of Na counterions from the sulfonic group of the latex particles. Dilutions were made in situ isoionically<sup>8</sup> so that linear reduced viscosity graphs were obtained. Two nitrogen driving pressures of 15 and 26 cm Hg were used, corresponding to total flow times of about 1200 and 700 sec, respectively, for water in the viscometers. The average shear rates calculated from Kroepelin's formula<sup>9</sup> were  $9,000$  and  $16,000 \text{ sec}^{-1}$ , respectively, over the range of concentrations used. Under such conditions, the corrections due to kinetic energy loss were less than 0.1% for the relative viscosity and were subsequently neglected in the calculation.

The reduced viscosities,  $\eta_{sp}/c$  obtained for the two fractions at different concentrations and ionic strengths are given in Tables I and II. Figures 2

and 3 present the same data in the conventional plots of viscosity. For comparison, additional data obtained for  $F_3$  at identical ionic strengths with a conventional Ubbelohde capillary viscometer<sup>10</sup> having an average shear rate of  $650 \text{ sec}^{-1}$  are included in Figure 3.

### REMARKS

The results for  $F_1$  have already been discussed in terms of the primary and secondary electroviscous effects of a charged colloid.<sup>1,2,7</sup> They are shown here, together with additional results for another fraction  $F_3$ , for the sole purpose of illustrating the use of these viscometers to measure low specific viscosities at moderately high shear.

As can be seen in Figure 3, since the problem of pressure variation was solved by the use of dual viscometers, the accuracy in the measurement of the specific viscosity should be the same as that for ordinary capillary viscometers. With the sulfonated latex, specific viscosities of down to 0.01 were determined with a precision of  $\pm 2\%$ . However, because of the smallness of the capillary radius ( $r = 0.1 \text{ mm}$ ), extra precaution was necessary to prevent the introduction of small dust particles into the viscometers. Also, the sorption effect,<sup>11</sup> though unobserved in the sulfonated latex, could limit its usefulness with certain polymeric materials, particularly at low concentration. By increasing the driving pressure, a shear rate of  $150,000 \text{ sec}^{-1}$  could be reached without the flow becoming turbulent.<sup>6</sup> But at such high shear, the accuracy of measurement would be lowered owing to the shorter flow times.

Finally, since the viscometer does not require an elaborate pressure control unit, it is easy to construct for common laboratory use. The simultaneous measurement of solvent and solution flow times makes such a viscometer most suitable for the determination of low specific viscosities. The fact that the test solution can be diluted in situ is especially attractive for investigating the concentration dependence of the viscosity at high shear rates.

The author is grateful to Dr. D. A. I. Goring for his helpful suggestions in this work.

### References

1. F. S. Chan and D. A. I. Goring, *J. Colloid Interfac. Sci.*, **22**, 371 (1966).
2. F. S. Chan, J. Blachford, and D. A. I. Goring, *J. Colloid Interfac. Sci.*, **22**, 378 (1966).
3. E. W. Merrill, *J. Polym. Sci.*, **38**, 539 (1959).
4. J. Schurz and E. H. Immergut, *J. Polym. Sci.*, **9**, 281 (1952).
5. S. H. Maron, I. M. Krieger, and A. W. Sisko, *J. Appl. Phys.*, **25**, 971 (1954).
6. S. Claesson and U. Lohmander, *Makromol. Chem.*, **44-46**, 461 (1961).
7. F. S. Chan, Ph.D. Thesis, McGill University, 1966.
8. D. T. F. Pals and J. J. Hermans, *Rec. Trav. Chim.*, **71**, 433 (1952).
9. H. Kroepelin, *Kolloid-Z. Z. Polym.*, **47**, 294 (1929).
10. A. W. Craig and D. A. Henderson, *J. Polym. Sci.*, **19**, 215 (1956).
11. O. E. Ohn, *J. Polym. Sci.*, **17**, 137 (1955).

Received November 17, 1970