Comparison of Relative Viscosity Measurement of Polyvinylpyrrolidone in Water by Glass Capillary Viscometer and Differential Dual-Capillary Viscometer

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ABSTRACT: The relative viscosity (RV) of polyvinylpyrrolidone (PVP) with different molecular weights was measured with a glass capillary viscometer and with a differential dual-capillary viscometer in water at different concentrations. For the differential dual-capillary viscometer, RV increases with a decreasing flow rate, especially for high molecular weight PVP at a 1% concentration. A good agreement in the RV between the two methods can be obtained for PVP with different molecular weights and at various concentrations if an appropriate flow rate is selected for the differential dual-capillary viscometer. Special precaution is needed when using the differential dual-capillary viscometer to measure the viscosity of a pure solvent. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1312–1315, 2002

Key words: viscosity; viscometer; shear; rheology; polyvinylpyrrolidone

INTRODUCTION

The relative viscosity (RV) determined from a dilute polymer solution using a glass capillary viscometer has been widely used for characterizing the molecular weight of a polymer for many decades.[1] Despite the significant advances in the technology of absolute molecular weight determination of polymers (such as light scattering) in the past few decades, RV is still indispensable in characterizing the molecular weight of a polymer due to its unsurpassed simplicity, sensitivity, and precision. There are many ASTM-approved test methods for polymers, based on the RV, in use today.[2]

Regardless of its simplicity, sensitivity, and precision, determination of the RV with a glass capillary viscometer requires meticulous experimental techniques and the viscometer must be thoroughly cleaned. Cleaning the viscometer with chromic acid is frequently needed. An automated capillary viscometer, which has been available since the 1980s, can save much time and effort in RV determination and improve precision.

The differential dual-capillary viscometer was invented and introduced in the 1980s to determine the RV of polymers. The principle of the differential dual-capillary viscometer has been thoroughly discussed in the patent literature and in ASTM-D-5225, Measuring the Solution Viscosity of Polymers with a Differential Viscometer.[3–5] Two recent articles discussed the advantages (such as precision, range, and sensitivity) of the differential dual-capillary method over the glass capillary viscometer.[6,7] However, these two articles reported differently on the agreement in the RV between the two methods.

In 1994, Hitchcock et al. reported excellent agreement in the RV determined by the differential dual-capillary viscometer and glass capillary viscometer or rotational viscometer for nylon (8.4% in formic acid).[6] However, in 2000, Abbott reported that, for nylon (8.4% in formic acid), the RV determined with a differential dual-capillary viscometer can be related to the RV determined with a glass capillary viscometer by a linear equation with a slope of 1.0029 and an intercept of 2.23.[7] In other words, the RV determined with a differential dual-capillary viscometer for nylon (8.4% in formic acid) cannot directly replace the RV determined with a glass capillary viscometer. It can be converted into the RV determined with a glass capillary viscometer according to a linear equation.

RV measured with a Cannon Fenske viscometer has been used at International Specialty Products (ISP) for the quality assurance of polymers for decades. In an effort to improve the operation in the quality-assurance laboratories at ISP, a differential dual-capillary viscometer was installed last year. This article reports some of the findings of the comparison of these two RV methodologies. To the best knowledge of the authors, no peer review article has been published comparing these two methods.

EXPERIMENTAL

A Schott AVS/G automated viscometer with an autosampler and with a Cannon Fenske size 75 viscom-

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TABLE I
RV of PVP Determined by Glass Capillary Viscometer and Differential Dual-Capillary Viscometer

		Glass viscometer		Differential viscometer			% Difference		
Grade	Concentration (%)	RV As is	RV, A with density correction	RV, B at 1.8 mL/min flow rate	RV, C at 0.86 mL/min flow rate	RV, D at 0.71 mL/min flow rate	A − B	A − C	A − D
K-15	5	1.5226 (0.0024)	1.5281 (0.0024)	1.5315 (0.0007)	1.5417 (0.0002)	1.5443 (0.0002)	−0.22	−0.89	−1.1
K-30	1	1.2583 (0.0034)	1.2611 (0.0029)	1.2604 (0.0002)	1.2654 (0.0016)	1.2663 (0.0006)	+0.06	−0.34	−0.4
K-60	1	1.2597 (0.0009)	2.0091 (0.0017)	1.9983 (0.0003)	2.0143 (0.0019)	2.0169 (0.0008)	+0.53	−0.26	−0.39
K-90	0.1	1.2130 (0.0009)	1.2133 (0.0009)	1.2120 (0.0004)	1.2200 (0.0003)	1.2210 (0.0005)	+0.11	−0.55	−0.63
K-90	1	4.5869 (0.0084)	4.5964 (0.0084)	4.4074 (0.0027)	4.5661 (0.0030)	4.5905 (0.0003)	+4.11	+0.66	+0.13

eter was used to measure the RV by the glass capillary method. A Viscotek Y501C relative viscometer with an autosampler and a 2-mL sample loop was used to measure the RV by the differential dual-capillary method. The inside diameter of the capillary of the Cannon Fenske size 75 viscometer is 0.54 mm, while the dimensions for the sample and reference capillaries are 0.02 in. (or 0.508 mm) in inside diameter and 24 in. in length for the Viscotek relative viscometer. The Viscotek relative viscometer is equipped with a gear pump and the flow rates used for this study are 1.8, 0.86, and 0.71 mL/min. An in-line filter was used for both viscometers.

Polyvinylpyrrolidone (PVP) made by free-radical polymerization by ISP were used in this study (Wayne, NJ). The typical weight-average molecular weights of the four grades of PVP used in this study are PVP K-15 (11,000), PVP K-30 (57,000), PVP K-60 (406,000), and PVP K-90 (1,270,000). 2-Butoxyethanol and ethylene glycol (EG) were reagent grade from Aldrich (Milwaukee, WI). Methanol and dimethylacetamide were HPLC grade from Aldrich.

Due to the difference in density between the solution (especially when the concentration is higher than 1%) and the solvent, for the Cannon Fenske viscometer, the RV should be calculated by dividing the product of the flow time of the solution and the density of the solution by the product of the flow time of the solvent and the density of the solvent. No density correction is needed for the differential dual-capillary method since the driving force of the flow is not due to gravity.[8] Therefore, in this study, for the Cannon Fenske viscometer, RV with a density correction was used to compare it with the RV determined by the Viscotek viscometer. In Tables I–IV, the numbers in parentheses are standard deviations of the respective RV.

TABLE II
RV of EG in Water

	Glass viscometer			
Sample ID	Flow time (s)	RV as is	RV with density correction	Viscotek RV 1.7 mL/min
10/90 EG/water	124.3 (0.2)	1.2515 (0.0012)	1.2677 (0.0012)	1.2651 (0.0013)
20/80 EG/water	156.7 (0.2)	1.5769 (0.0015)	1.6180 (0.0016)	1.6227 (0.0013)
30/70 EG/water	199.2 (0.1)	2.0042 (0.0013)	2.0832 (0.0014)	2.0884 (0.0017)
40/60 EG/water	255.4 (0.1)	2.5685 (0.0001)	2.7039 (0.0001)	2.7055 (0.0025)
50/50 EG/water	330.9 (0.2)	3.3292 (0.0017)	3.5470 (0.0018)	3.5348 (0.0031)
60/40 EG/water	434.5 (0.2)	4.3710 (0.0025)	4.7089 (0.0027)	4.6993 (0.0020)
70/30 EG/water	584.5 (0.3)	5.8797 (0.0028)	6.3983 (0.0031)	6.3728 (0.0038)
EG	1667.1 1667.1	16.7716 16.7716	18.6282 18.6282	8.3214 (0.26)

TABLE III
RV of Dimethylacetamide and 2-Butoxyethanol

Sample ID	RV Viscotek	RV Cannon Fenske
Dimethylacetamide	1.0301 (0.0191)	1.102 1.101
2-Butoxyethanol	3.0808 (0.0323)	3.482 3.478 3.478

RESULTS AND DISCUSSION

RV of PVP in water

According to the U.S. Pharmacopoeia (USP), the RV of PVP should be determined from 0.1% (PVP K-120), 1% (PVP K-30, 60, and 90), and 5% (PVP K-15) solutions in water.[9] For PVP in pharmaceutical application, changing the RV methodology from a glass capillary viscometer specified in the USP to a differential dual-capillary viscometer requires cross-validation.

As shown in Table I, at the 1.8-mL/min flow rate for the Viscotek viscometer, the RVs determined by the two methods (columns 4 and 5) are in good agreement (difference less than 0.6%) for PVP K-15, K-30 (1%), K-60 (1%), and K-90 (0.1%). For the high molecular weight grade PVP at 1%, the RV determined by the differential dual-capillary viscometer is lower by about 4%. In other words, at the 1.8 mL/min flow rate for the Viscotek viscometer, for low and medium molecular weight PVP and for high molecular weight PVP at 0.1%, the RV determined by the differential dual-capillary viscometer can be a direct replacement for the RV determined by the glass capillary viscometer. For high molecular weight PVP at 1%, a correlation factor, which is dependent on the molecular weight, is needed to convert the RV determined by the differential dual-capillary viscometer to the RV determined by the glass capillary viscometer.

The lower RV determined by the differential dual-capillary viscometer for the high molecular weight PVP at the 1.8 mL/min flow rate is not caused by shear degradation, because the molecular weight distribution of the sample eluted from the viscometer overlaid well with the original sample (Fig. 1). The weight-average molecular weight of the original PVP K-90 and after elution from the Viscotek viscometer are 772,000 and 750,000, respectively [relative to poly(ethylene oxide) standards]. Furthermore, the RV determined for the high molecular weight PVP at 0.1% agrees well with the RV determined by the glass viscometer. The shear rate is the same for the 1% PVP solution and the 0.1% PVP solution, since the flow rate is the same. To further explore the cause of this problem, the experiments in the next two sections were carried out.

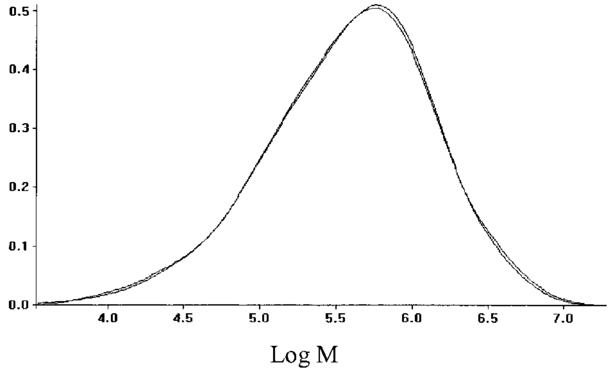

Figure 1 Overlay of molecular weight distribution of PVP K-90 before and after elution from Viscotek viscometer.

RV of EG in water

The results in Table II show that the RV of EG in water determined by the differential dual-capillary viscometer is the same (difference less than 0.2%) as that of the RV measured by the Cannon Fenske viscometer (after correction for the difference in density between the EG/water mixture and water) up to 70% EG (RV = 6.3983). This demonstrates the linearity of the response of the differential dual-capillary viscometer. The lower RV reported by the differential dual-capillary viscometer for high molecular weight PVP at 1% is not due to a nonlinear response of the differential dual-capillary viscometer at high RV.

Surprisingly, it was noticed in Table II that the differential dual-capillary viscometer severely under-

TABLE IV
RV of High Molecular Weight Grade PVP in Water at Different Concentrations

Concentration (%)	RV (Cannon Fenske), A	RV (Viscotek), at 1.7 mL/min, B	%, Difference, A − B
0.1	1.2140 (0.0020)	1.2093 (0.0003)	0.39
0.3	1.7490 (0.0014)	1.7230 (0.0006)	1.49
0.5	2.4117 (0.0040)	2.3415 (0.0011)	2.91
0.6	2.7863 (0.0023)	2.7062 (0.0048)	2.87
0.7	3.1897 (0.0023)	3.0746 (0.0042)	3.61

estimates the RV of pure EG. Similar behavior is also noticed for the RV of other pure solvents which are miscible with water (the mobile phase used in the dual-capillary viscometer), such as dimethylacetamide and 2-butoxyethanol in Table III. Furthermore, RV readings themselves are not reproducible for pure solvents, as indicated by the large standard deviations. The exact cause for the problem is not known. It should not be due to mixing or dilution in the viscometer, as the RV of the polymer solution can be determined accurately. It should not be due to shear thinning, since the low molecular weight solvents should be Newtonian fluids. There is probably a problem with the heat of mixing between the solvent and the mobile phase.[10] The fact that the RV continues to decrease with repeated injections seems to support this explanation. This problem was not discussed in ASTM D 5225.

Flow rate and concentration dependency of RV of high molecular weight PVP measured by the differential dual-capillary viscometer

The results in Table I show that, as the flow rate decreases, the RV measured by the differential dual-capillary viscometer increases. However, there is no discussion on the dependence of the RV on the flow rate in ASTM D 5225, Measuring Solution Viscosity of Polymers with a Differential Viscometer. The effect of the flow rate on the RV is much more pronounced for the high molecular weight PVP than for the low and medium molecular weight PVP. As demonstrated in Table IV, the percent difference in the RV for the high molecular weight PVP increases with an increasing concentration. Therefore, the lower RV for high molecular weight polymers measured at a 1.8 mL/min flow rate is attributable to the shear thinning or non-Newtonian behavior of the 1% solution of the high molecular weight PVP.[6]

The flow times for water, 5% PVP K-15, 1% PVP K-30, 1% PVP K-60, 1% PVP K-90, and 0.1% PVP K-90 for the Cannon Fenske size 75 viscometer are 99, 151, 125, 199, 456, and 120 s, respectively. For the Schott AVS/G automated viscometer, the volume of the solution delivered into the Canon Fenske viscometer is 7.5 mL. Therefore, the average flow rates for the PVP K-15, K-30, K-60, K-90 (1%), and K-90 (0.1%) solutions through the Canon Fenske size 75 viscometer are 2.99, 3.61, 2.26, 0.99, and 3.75 mL/min. As shown in Table I, the difference in the RV between the two methods for the 1% high molecular weight PVP solution decreases from about 4 to 0.8 and 0.3% as the flow rate used for the differential dual-capillary viscometer decreases from 1.8 to 0.86 and 0.71 mL/min.

In other words, to have good agreement in the RV between the two methods for the high molecular weight PVP at 1%, the flow rate used for the differential dual-capillary viscometer (0.86 or 0.71 mL/min) should be close to the flow rate (0.99 mL/min) for the Canon Fenske size 75 viscometer. Overall, less than a 1% difference in the RV between the two methods for all molecular weight grades of PVP and at all concentrations can be achieved if a flow rate of 0.86 mL/min is used for the differential dual-capillary viscometer.

The results in Table I also show that the differential dual-capillary viscometer is very sensitive and precise in the RV measurement, especially at low concentrations. Therefore, the use of a low concentration (e.g., 0.1%), especially for high molecular weight polymers, can eliminate the difference in the RV between the two methods.

CONCLUSIONS

For the differential dual-capillary viscometer, the RV increases with a decreasing flow rate, especially for high molecular weight PVP at 1% concentration. The RV determined by the differential dual-capillary viscometer can be used as a direct replacement for the RV determined with a glass capillary viscometer for all molecular weight grades of PVP and at all concentrations if a low flow rate of 0.86 mL/min is used for the differential dual-capillary viscometer. The use of a low concentration (e.g., 0.1%), especially for high molecular weight polymers, can also eliminate the difference in RV between the two methods. A differential dual-capillary viscometer should be used with precaution to measure the RV of a pure solvent.

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