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SHORT COMMUNICATION

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A polytetrafluoroethylene capillary viscometer

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Abstract A polytetrafluoroethylene (PTFE) capillary Ubbelohde viscometer was designed and constructed. The relative viscosities of aqueous solutions of a polyethylene oxide and a polyvinylpyrrolidone sample were carefully determined down to an extremely dilute concentration region. In comparison with the data obtained from the common glass capillary viscometer, slippage is believed to occur in the PTFE capillary due to its hydrophobic nature. While for the glass capillary viscometer, conventional viscous flow is operative and adsorption phenomena occur since both the solvent water and aqueous solution are wet and/or adsorbed onto the glass capillary surface due to the existence of hydroxyl groups on glass surface. The data were analyzed with a recently developed wall-effect theory and satisfactory results were obtained.

Keywords PTFE viscometer · Polymer solution · Viscosity · Viscosity measurement

Introduction

Recently, considerable attention has been devoted to viscosity measurements on polymer solutions down to an extremely dilute concentration region [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. Lots of experimental results and theoretical predications have indicated that there exists a boundary concentration C_s between extremely dilute and dilute concentration regions [9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19]. In the extremely dilute concentration region, polymer chains exist in isolated state and only intra-chain interactions operate, while in the dilute concentration region interchain interactions are introduced. The boundary concentration C_s is commonly very low (10^{-4}–10^{-3} g/mL) [14, 15, 16, 17, 18, 19], therefore viscosity measurements have to be performed on polymer solutions with relatively low concentration to identify and measure this concentration. However, as the viscosity measurements are performed on polymer solutions in the extremely dilute concentration region, another serious problem arises; the linear relationship between reduced viscosity η_{sp}/C and concentration no longer exists. This is ascribed to the viscometer capillary wall effects [1, 2, 3, 4, 5, 6, 7, 8, 20, 21, 22, 23, 24, 25]. Based on the idea of wall effects on viscosity measurements of polymer solutions, Cheng et al. [1, 2, 4] have given a quantitative theoretical expression; it could well describe the concentration-dependence of polymer solution viscosity from dilute down to the extremely dilute concentration region.

For the conventionally used glass capillary viscometer, adsorption phenomena are unavoidable in measuring viscosity due to the existence of hydroxyl groups on the glass capillary inner surface. Changing the surface property, by coating paraffin on a glass capillary viscometer, causes slippage to occur for aqueous solutions [5], due to its hydrophobic nature. However, paraffin cannot be coated firmly and permanently. In the present work, the capillary of a Ubbelohde viscometer was replaced by a polytetra-fluoroethylene capillary, by which the solute adsorption may be expected to be eliminated since its hydrophobic properties are similar to paraffin. We measured the viscosities of aqueous solutions of polyethylene oxide (PEO) and polyvinylpyrrolidone (PVP) in this viscometer and compared the results with those obtained with a conventional glass capillary viscometer. The difference between the two sets of data clearly shows that the flow mode is inverted from viscous to slip flow as the glass capillary is replaced by Teflon capillary. In this paper, we describe a new tool (the PTFE capillary viscometer) for helping to understand the contribution of wall effects to the experimental viscosity abnormalities that appear in the extremely dilute concentration region in usual viscosity measurements of polymer solutions. This has been done by determining and comparing the viscosity of the same sample solution in both glass and PTFE capillary viscometers.

Experimental

Samples

The PEO sample, which had been synthesized with carbonated alkaline-earth metals as catalysts, was kindly provided by Prof. Liansheng Jiang of the Changchun Institute of Applied Chemistry, Chinese Academy of Sciences. Weight average molecular weight (M_w) of PEO is 3.9×10^5, $M_w/M_n=2.0$.

The PVP sample used in this work was a commercial product of BASF. Weight average molecular weight (M_w) is 6.1×10^4, $M_w/M_n=2.81$.

Viscometers

The glass capillary part of the conventional Ubbelohde viscometer was displaced by a Teflon capillary using a special method [26]. The inner diameter of the PTFE capillary is 0.573 mm, and that of the glass capillary is 0.395 mm. To completely clean the viscometers, the cleaning work must be careful. To clean the glass viscometers, we first soaked them in chromic acid mixture for a day, rinsed the viscometer repeatedly with deionized distilled water, then rinsed the glass viscometer with boiled deionized distilled water under ultrasonic conditions, and finally the cleaned glass viscometers were dried in a common oven at 125 °C. To clean the PTFE capillary viscometer, the cleaning procedures were the same except for omission of the soaking in chromic acid mixture. The thoroughly cleaned PTFE capillary viscometer was dried in a vacuum oven at 85 °C.

Viscosity measurements

Aqueous stock solutions of the PEO and PVP samples with higher concentration were freshly prepared by weighing and filtering through a sintered G5 filter to remove the dust. According to the method suggested previously in our laboratory [4, 5], the viscosity measurements of aqueous solutions of PEO and PVP were performed using a stopwatch with measured accuracy of 0.01 s at 30 ± 0.05 °C, according to the sequence from low to high concentration. Firstly pure solvent (water) with a known weight was transferred into the viscometer and its efflux time was measured for every experiment. The constancy of the solvent efflux time serves as a criterion for judging the consistency of experimental conditions and the state of the viscometer. The efflux times of water in the glass and PTFE capillary viscometers at 30 °C are 358.42 s and 158.21 s, respectively. After measuring the efflux time of solvent, a definite amount of weighed stock sample solution with known higher concentration was added into the viscometer. A syringe was used to produce air purge to well mix the solution in the viscometer. The efflux time of the solution was measured after about half an hour. This operation was repeated successively until the relative viscosity reached a predetermined point. The constancy of the flow time of the measured solution can be used to judge whether the solution has been mixed well. The reproducibility of the flow times for the well mixed solution was almost excellent. The experimental error of the flow time could be controlled within ±0.03 s The flow time given in this present script is the arithmetic average value of more than six measured flow times. The ratio of the efflux time of solution t_{solu} to that of solvent t_{solv} was regarded as the experimental relative viscosity, $\eta_r=t_{solu}/t_{solv}$. The obtained weight concentration in g/g of the solution was converted to weight-volume concentration in g/mL by applying the density correction.

The technique of preparing the solution by weighing with increasing concentration, instead of diluting, has several advantages. Besides getting higher accuracy of concentration and more data points lying in the low concentration range, the weighing method avoids the problem raised by endless increasing of solution volume in the viscometer upon dilution. Furthermore, the problems caused by the lower rate of desorption at low concentration for polymers adsorbed at higher concentration may also be eliminated.

Results and discussion

The most distinct difference between the measured relative viscosities with the two viscometers appears in the extremely dilute concentration region of $\eta_r<1.1$ as shown in Fig. 1. The relative viscosities measured in the PTFE capillary viscometer are always somewhat lower than those measured in glass viscometer for same concentration solutions. In this concentration region, the plots of η_r versus C exhibit good linearity for both viscometers. Apparent linear regression analyses yield nearly perfect straight lines with correlation coefficients R greater than 0.9999 and similar slope B. However, the intercept A is more than 1.0 for the experimental data measured in the glass viscometer, while it is less than 1.0 for the data measured in the PTFE capillary viscometer, as shown in Fig. 1 and Table 1. The fact that the linear regression lines do not pass through the origin coordinate (0,1) indicates that there exists systematic interference due to interfacial interaction between the flowing solution and the capillary inner surface.

The interfacial phenomena during measurement of the viscosity of polymer solutions using a glass capillary viscometer are unavoidable. Probably it is the most serious source of error, especially in the

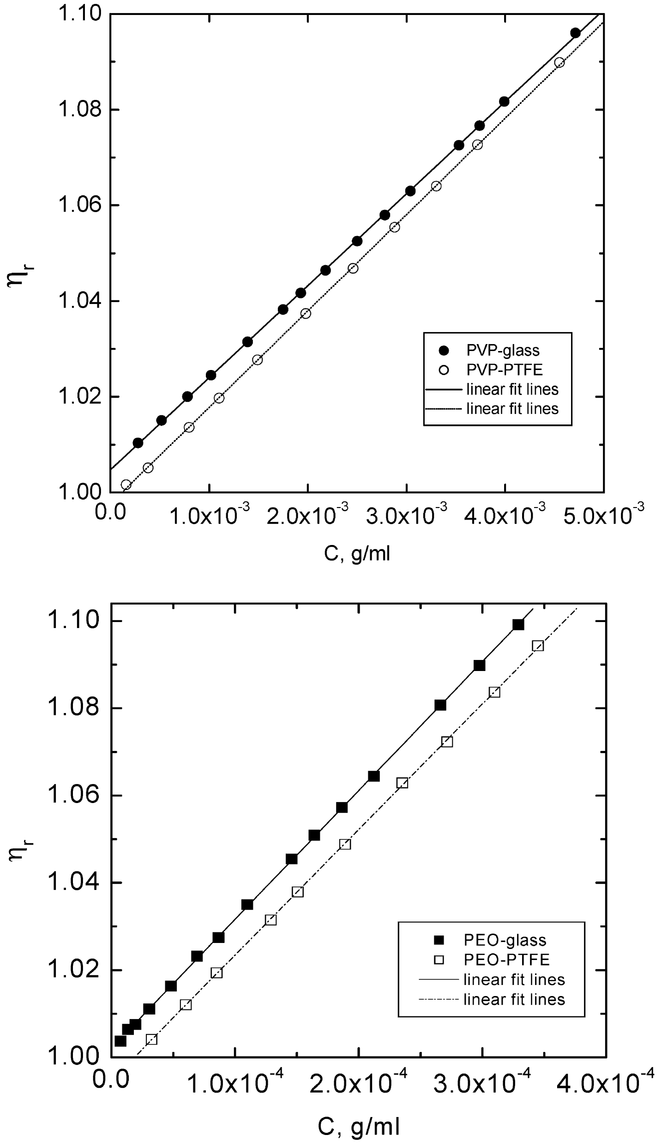

Fig. 1 Concentration dependence of experimental relative viscosity of aqueous PVP and PEO solutions in the extremely dilute concentration region for $\eta_r < 1.1$ measured by viscometers with glass (*filled points*) and PTFE (*open points*) capillaries

Table 1 Linear regression coefficients of the relative viscosity versus concentration in the extremely dilute concentration region

Viscometer	Polymer	A	B	R
Glass	PVP	1.00477	19.2305	0.99994
	PEO	1.00213	295.2174	0.99994
PTFE	PVP	0.99766	20.1436	0.99993
	PEO	0.99468	287.7019	0.99995

extremely dilute concentration region of polymer solution. We have deduced that the experimental relative viscosity $\eta_{\mathrm{r,exp}}$ should be related to the true relative viscosity $\eta_{\mathrm{r,true}}$ of polymer solution by a simple equation [2, 3, 4, 5]

$$\eta_{r,\exp} = f_{\mathrm{int}} \cdot \eta_{r,true} \tag{1}$$

where the pre-factor f_{int} denotes the contribution of interfacial effects and may be regarded as a correction factor, and expressed as [2, 3, 4, 5]

$$f_{\mathrm{int}} = 1 + \frac{k \cdot C}{C_a + C} \tag{2}$$

The parameter k in Eq. 2 describes the nature and the extent of the interfacial interaction. In the case of viscous flow, both solvent and solute molecules are adsorbed onto the capillary wall surface, yielding a positive k. The magnitude of k correlates to the thickness of the adsorbed layer on the capillary. The parameter C_a is the characteristic concentration at which the coverage of solute on the capillary wall surface just equals 0.5. If the solvent does not wet the capillary surface, slippage of the solution would occur and would yield a negative k. In this circumstance, adsorption cannot take place and, thus, C_a will be zero [5].

The true relative viscosity $\eta_{\mathrm{r,true}}$ of dilute polymer solutions can be best represented by [2, 4, 8]

$$\eta_{r,true} = 1 + [\eta] \cdot C + 6 \cdot K_m \cdot [\eta] \cdot C^2 \tag{3}$$

instead of the conventionally used Huggins equation:

$$\eta_{r,true} = 1 + [\eta] \cdot C + k_H \cdot [\eta]^2 \cdot C^2 \tag{4}$$

In Eq. 3, the apparent self-association constant K_m, which is related to the sizes and interactions between polymer chains in solution, can be mutual convertible with the Huggins slope constant as

$$K_m = \frac{k_H \cdot [\eta]}{6} \tag{5}$$

deduced from a consideration of cluster formation due to the existence of the interactions between polymer chains in solution [2, 8] and correlates with the dynamic contact concentration C_s as

$$C_s = \frac{0.001}{2K_m} \tag{6}$$

Combing Eqs. 1, 2 and 3, we have

$$\eta_{r,\exp} = (1 + \frac{k \cdot C}{C_a + C}) \cdot (1 + [eta] \cdot C + 6 \cdot K_m \cdot [\eta] \cdot C^2) \tag{7}$$

By the traditional usage, the experimental reduced viscosity

$$\left(\frac{\eta_{sp}}{C}\right)_{\exp} = \frac{\eta_{r,\exp} - 1}{C} \tag{8}$$

should be expressed by

$$\left(\frac{\eta_{sp}}{C}\right)_{\exp} = \frac{k}{C_a + C} + \left(1 + \frac{k \cdot C}{C_a + C}\right) \cdot ([\eta] + 6 \cdot K_m \cdot [\eta] \cdot C) \tag{9}$$

Equation 8 indicates that the plot of experimental reduced viscosity versus concentration is no longer linear. It may bend upward or downward in the extremely dilute concentration region depending on whether the interfacial parameter k is positive or negative.

The plots of reduced viscosity versus concentration of PVP and PEO are shown in Fig. 2. In the extremely dilute concentration region, the curve of the reduced viscosity measured by the viscometer with a PTFE capillary bends downwards in contrast to that measured by the glass viscometer. Then, a problem naturally appears: to what degree do the errors of the measured flow times affect the curvatures of the plots in the extremely dilute concentration region? Therefore, we compared the reduced viscosities calculated from the maximum and minimum flow times (indicated by the dashed line) and those calculated from the average flow time for the same concentration, as shown in Fig. 2. The following two facts were found:

1. In the measured concentration range, the discrepancy between the reduced viscosities calculated from the maximum and minimum flow times decreases with increasing concentration, and coincides in the higher measured concentration range. It is reasonable that in the very low concentration region for the same measured error of flow time,the smaller the concentration, the greater the discrepancy between the reduced viscosities calculated from the maximum and minimum flow times.
2. The errors do not change or even strikingly affect the curvatures of the plots of reduced viscosity versus concentration in the extremely dilute concentraton region, obtained in either glass or PTFE capillary viscometers.

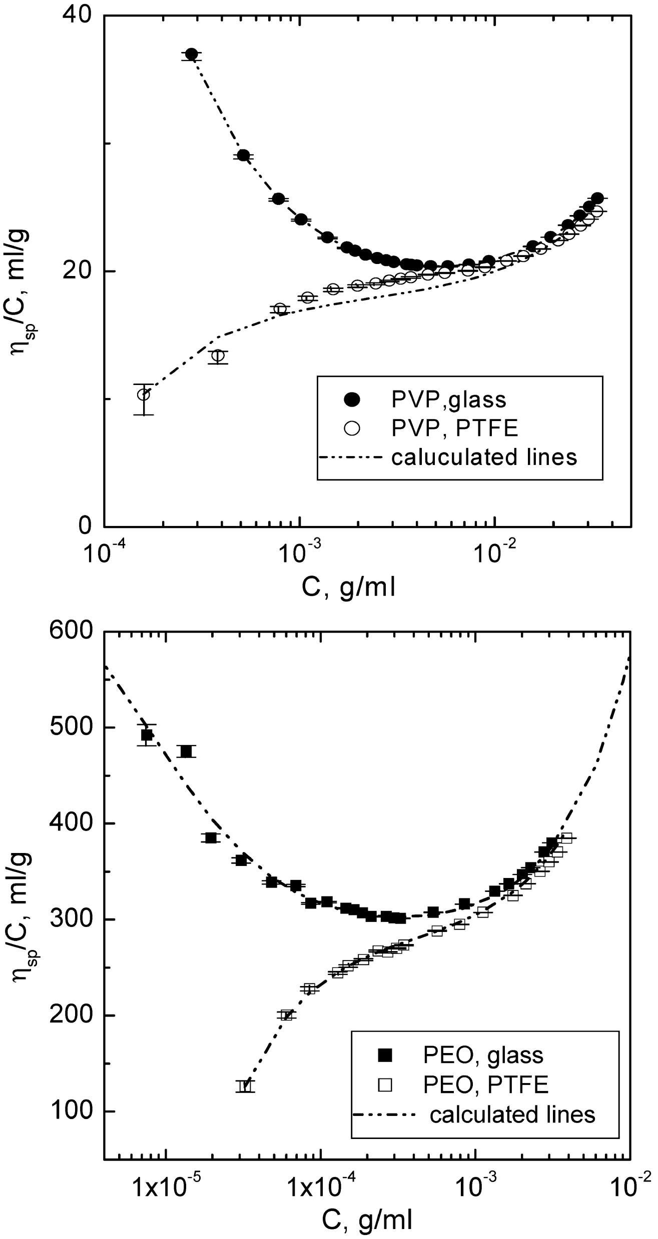

Fig. 2 Semi-logarithmic plots of reduced viscosity versus concentration for aqueous solutions of polyethylene oxide (PEO) and polyvinylpyrrolidone (PVP) in glass and PTFE capillary viscometers. The *dotted lines* were calculated according to Eq. 8. *Dashed lines* (–) were calculated from the measured maximum and minimum flow times for the same concentration solution; ■, □, ●, ○ were calculated from the average flow times

Therefore, a conclusion can be naturally reached that the viscosity abnormalies observed in the very dilute concentration region in this script cannot be attributed to measurement errors. The distinct difference of plots of reduced viscosity versus concentration in the extremely dilute concentration range (as shown in Fig. 2) should be ascribed to another reason, that is to say, wall effects. It also clearly demonstrates that the flow mode of the aqueous solution changes from viscous flow to slippage as the glass capillary is replaced by PTFE capillary [5]. By an iterative fitting procedure to treat the reduced viscosity data calculated from the average flow times according to Eq. 8, the parameters [η], K_m, k, and C_a were obtained. The results are listed in Table 2. The calculated curves of reduced viscosity using these parameters are also drawn in Fig. 2. The coincidence of the curves with the experimental points is excellent. It demonstrates that the observed reduced viscosity data could be precisely described by Eq. 8. If taking f_{int} as a correction factor, the corrected relative viscosity equals the experimental relative viscosity divided by f_{int}. The corrected reduced viscosity ver-

Table 2 Viscosity parameters of aqueous solutions of PVP and PEO measured by viscometers with a glass capillary and a PTFE one, respectively

Polymer	Viscometer	$[\eta]$ (mL/g)	K_m	k	C_a (g/mL)	C_s (g/mL)	b_{eff} (nm)	Δb_{ex} (nm)
PEO	Glass	282.1	17.3	0.00337	7.9×10^{-6}	2.89E-5	166	
	PTFE	282.1	17.3	−0.00505	0	2.89E-5		352
PVP	Glass	17.91	2.06	0.0062	5.0×10^{-5}	2.43E-4	305	
	PTFE	17.91	2.06	−0.0012	0	2.43E-4		59

sus concentration plots thus obtained for the two viscometers with different flow modes coincide with each other to one straight line as shown in Fig. 3. This straight line obeys

$$\frac{\eta_{sp}}{C} = [\eta] + 6 \cdot K_m \cdot [\eta] \cdot C \tag{10}$$

It represents the theoretical true reduced viscosity of the polymer solution.

The dynamic contact concentration C_s evaluated from the apparent association constant K_m by Eq. 6 for the samples of PVP and PEO are listed in Table 2. It indicates that the Cs of PEO is lower than that of PVP in aqueous solution. The result is reasonable since the molar weight of PEO is higher than that of PVP and is in accordance with the results observed by Craubner [27, 28] who observed that the higher the molar mass, the lower the critical concentration, Although the definition of the dynamic contact concentration C_s is possibly different from the definition of the critical concentration.In usual viscosity measurement the critical concentration is the concentration at which a relative minimum reduced viscosity is observed [27, 28], and the C_s in Eq. 6 is defined as the concentration at which the concentration of the polymer aggregates in solution is one in a thousand of that of all polymer chains in solution [2]. In our other paper [4], we have obtained the dynamic contact concentration C_s of polystyrene(PS) in benzene calculated by Eq. 6, which varied from 1.64×10^{-5}g/mL to 3.38×10^{-4}g/mL for PS with weight-average molecular weight $Mw = 2.24\times10^4$–1.69×10^6. The C_s values of PEO and PVP fall in the concentration range of C_s of polystyrene in benzene. However, the C_s concentrations obtained in this script and another paper [4] are somewhat lower than those obtained by other different techniques such as gel permeation chromotography (GPC) [14], excitated fluorescence spectrometry (EFM) [18],and dynamic light scattering (DLS) [19].

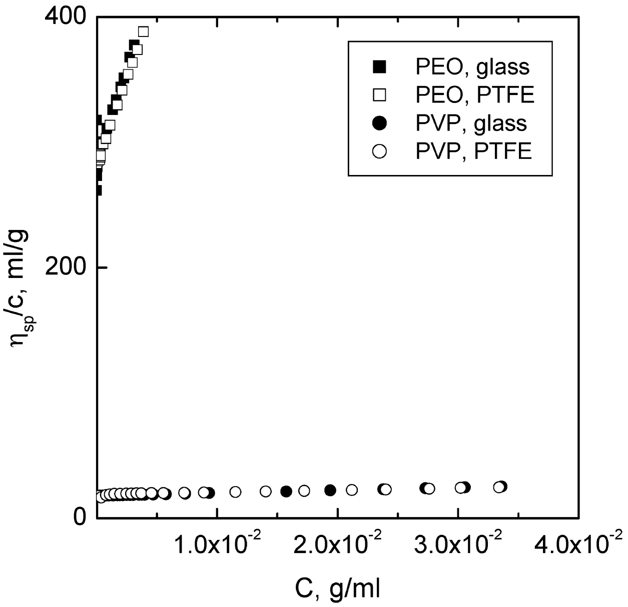

Fig. 3 Plots of corrected reduced viscosity versus concentration

Regarding the interfacial interactions, in the case of adsorption possessing a positive k, an effective adsorption layer thickness could be deduced according to the formula [4]:

$$b_{eff} = R \cdot \left(1 - \frac{1}{(1+k)^{\frac{1}{4}}}\right) \tag{11}$$

where R is the inner radius of the capillary. For a negative k, which indicates that the flow mode of solvent and solution is slip flow, a difference of extrapolation length could be evaluated by [5]:

$$\Delta b_{ex} = -\frac{k \cdot R}{4} \tag{12}$$

The obtained results are also summarized in Table 2. The magnitudes of these lengths are reasonable and should be related to the conformation of the macromolecule near the capillary surface. However, a quantitative interpretation needs more systematic data, which include viscosity data (obtained from the newly-made Teflon capillary and commonly used glass capillary viscometers) of macromolecule solutions by changing variables such as molecular mass, solvent, temperature, capillary radius, and macromolecular chemical structure, i.e, different soft and hard backbone chain, side group, etc.

Conclusion

In this script we present a new capillary viscometer with surface properties different from the conventional glass capillary viscometer. Since the properties of the PTFE surface and the glass surface of the used viscometers are stable before and after viscosity measurements on polymer solutions, it become practicable to systematically study interfacial phenomena occurring between the fluids flowing in viscometers and the inner surfaces of the capillaries with hydrophobic and hydrophilic properties during viscosity measurements.

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