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The wall effect on viscosity measurement of dilute aqueous solutions of polyethylene glycol and polyvinyl alcohol using a paraffin-coated capillary viscometer

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Abstract

The relative viscosities of aqueous solutions of a polyethylene glycol sample and a polyvinyl alcohol sample were measured in a viscometer, the capillary wall surface of which was coated with paraffin. The results were compared with the data obtained from the original non-coated viscometer. Slippage occurs in the former case due to the hydrophobic nature of paraffin, while in the latter case, conventional viscous flow operates since both the solvent water and solution either wet and/or are adsorbed on to the glass capillary surface of the viscometer. The experimental data were analyzed with the aid of the recently proposed theory of the effect of solute adsorption on relative viscosity measurements. The formula, accounting for the effect of solute adsorption of polymer solutions down to the extremely dilute concentration region, are also applicable to non-wetting polymer solutions in which solute adsorption is eliminated. The results obtained were compared and analyzed using the idea of extrapolation length of slip flow proposed by de Gennes PG. CR Acad Sci Paris 1979;288B:219. The extrapolation length could be evaluated unambiguously from the relative or reduced viscosity data for polymer solutions down to the extremely dilute concentration region.

Keywords: Wall effect; Slippage; Solute adsorption

1. Introduction

Viscous capillary flow in viscometry is firmly established both theoretically and experimentally [1,2]. It is generally assumed that a flowing liquid completely wets the capillary wall surface such as in the case of water, which wets the glass surface and provides a zero contact angle. In measuring the viscosity of a solution, an additional problem arises. Is the solute wet or can it be adsorbed into the surface of the glass capillary wall? The answer is certainly yes. Recently, the effect of solute adsorption on relative viscosity measurements has been studied quantitatively [3–5]. The proposed theoretical formula could satisfactorily describe the concentration dependence of the viscosity of a polymer solution down to the extremely dilute concentration region. If the solvent does not wet the capillary wall surface, naturally one may expect that adsorption would not occur both for the solvent and solute, and slip flow should exist under such conditions. The slip flow of polymer solutions has been extensively studied [6–13] in the literature; however, investigations on extremely dilute polymer solutions are comparatively rare. In the present work, we measure the viscosity of aqueous solutions of polyethylene glycol (PEG) and polyvinyl alcohol (PVA) in a paraffin-coated viscometer and discuss the obtained results with regard to wall effects such as solute adsorption and slippage, by comparison with data obtained from the original non-coated viscometer.

2. Experimental

2.1. Materials

A commercial PEG sample with $M_n = 21090$, $M_w/M_n = 1.75$ and a PVA sample with DP = 1750 were used for this study. Aqueous stock solutions of these two samples were prepared by weighing and filtering through a Millipore filter to remove the dust for viscosity measurements.

2.2. Viscosity

A dilution-type suspended level glass viscometer with

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capillary diameter 0.442 mm was used. All viscosity measurements were carried out at 25 ± 0.05°C. The flow time of a known weight of pure water in the clean untreated viscometer was first measured. Afterwards, an aqueous PEG stock solution with known weight concentration was added successively into the viscometer by weighing, in order to increase the solution concentration in the viscometer. The weight concentration was converted into a weight–volume concentration (in g/ml) by applying density corrections to the solution. The flow times for each solution with different concentration in the viscometer were measured. The ratio of flow time of solution to that of solvent was regarded as the relative viscosity. After finishing the solution viscosity measurements, the viscometer was thoroughly cleaned and dried. Next, a solution of paraffin in ethyl ether of 2.25×10^{-4} g/ml concentration was introduced into the wide bore tube of the vertically-held viscometer until the solution reached a position higher than the upper orifice of the capillary and below the lower mark of the measuring bulb. After standing for a while, the paraffin solution was withdrawn from the wide bore tube of the viscometer. The viscometer was then dried under vacuum. Following the same procedure, the relative viscosity of the aqueous PEG solution was again measured in this paraffin-coated viscometer. After finishing the viscosity measurements for the aqueous PEG solution, the viscometer was thoroughly cleaned to remove the paraffin coating and the relative viscosity of the aqueous PVA solution was again measured using the same procedure as described above for the PEG solution.

3. Results and discussion

The measured flow times of water at 25°C through the viscometer, before and after paraffin coating, were 290.80 s and 313.59 s for the first run for measuring the relative viscosity of the PEG solution and 290.85 s and 323.56 s for the second run for measuring the relative viscosity of the PVA solution. These flow times for pure solvent (water) are designated as $t_0(0)$ and $t_{0,\mathrm{coat}}(0)$, respectively. The subscript 0 in these symbols denotes pure solvent and the zero in parentheses denotes flow time measurements taken for the clean viscometer. The slight difference between $t_0(0) = 290.80$ for the first run for measuring PEG solution and $t_0(0) = 290.85$ for the second run for measuring PVA solution is probably due to a difference in the actual temperature or the alignment of the viscometer. The flow time $t_{0,\mathrm{coat}}(0)$ is longer than $t_0(0)$ because the paraffin coating produces a reduction in the radius of the capillary. Designating the effective thickness of paraffin coat layer as b_{coat} and applying Poiseuille's equation, we have

$$\eta_0 = (\pi \rho_0 g h / 8VL) R^4 t_0(0) \tag{1}$$

for the original viscometer and

$$\eta_0 = (\pi \rho_0 g h / 8VL)(R - b_{\mathrm{coat}})^4 t_{0,\mathrm{coat}}(0) \tag{2}$$

for the viscometer after paraffin coating. Where η_0 and ρ_0 are the viscosity and density of the pure water, L is the length of the capillary, V is the volume of the measuring bulb, R is the radius of the capillary before paraffin coating. Since the inner wall surface of the measuring bulb was not coated with paraffin, V remains constant and the effective radius of the capillary changes from R to $(R - b_{\mathrm{coat}})$. Expressing the change of flow time of water due to paraffin coating by a coefficient k_{coat} defined as

$$k_{\mathrm{coat}} = \frac{t_{0,\mathrm{coat}}(0) - t_0(0)}{t_0(0)} \tag{3}$$

and combining Eqs (1), (2), we have

$$b_{\mathrm{coat}} = R\left(1 - \frac{1}{(1 + k_{\mathrm{coat}})^{1/4}}\right). \tag{4}$$

The effective coat layer thickness of paraffin thus obtained equals 0.004124 mm for the first run and 0.005811 mm for the second run. The latter is 1.4 times thicker than the former.

The relative viscosities of these two aqueous solutions with various concentrations before and after paraffin coating were calculated from the flow time of solution measured in the viscometer by dividing it by the corresponding flow time of water. The results obtained are listed in Table 1. The relative viscosities, measured using the paraffin-coated viscometers, are somewhat lower than those measured using the original viscometer for the same concentration as shown in Fig. 1. Furthermore, they are less than one for the most dilute solutions measured, though they still increase

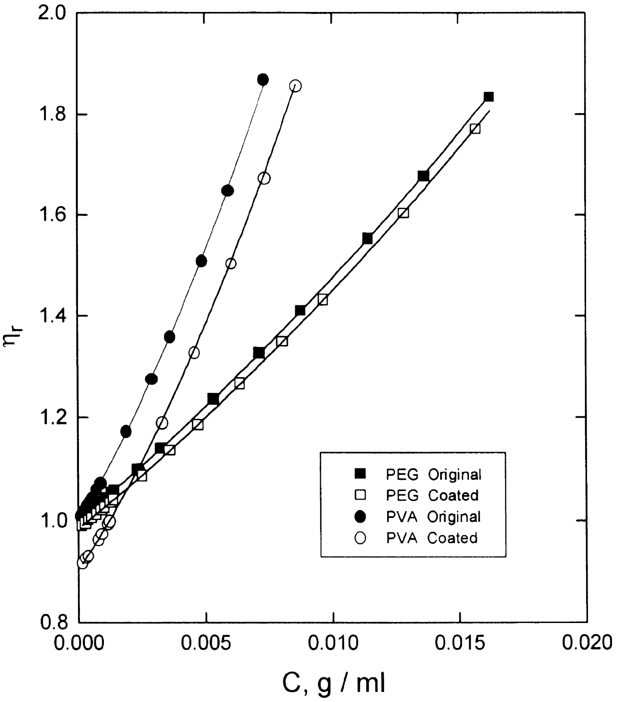

Fig. 1. Effect of capillary surface coating with paraffin on the relative viscosity of aqueous solution of PEG and PVA.

Table 1
The relative viscosities of aqueous solutions of polyethylene glycol and polyvinyl alcohol measured in a viscometer before and after its capillary wall surface coated with paraffin

Polyethylene glycol Original viscometer		Paraffin coated		Polyvinyl alcohol Original viscometer		Paraffin coated	
C (g/ml)	η_r	*C* (g/ml)	η_r	*C* (g/ml)	η_r	*C* (g/ml)	η_r
1.539E-4	1.0080	1.604E-4	0.9910	9.85E-5	1.0088	1.63E-4	0.9174
2.767E-4	1.0131	2.685E-4	0.9956	1.712E-4	1.0143	2.979E-4	0.9268
4.102E-4	1.0182	4.052E-4	1.0008	2.449E-4	1.0206	3.860E-4	0.9306
5.255E-4	1.0229	5.326E-4	1.0054	3.557E-4	1.0300	5.402E-4	0.9432
6.642E-4	1.0286	7.270E-4	1.0136	4.363E-4	1.0364	7.899E-4	0.9630
8.295E-4	1.0354	9.028E-4	1.0204	5.347E-4	1.0449	9.274E-4	0.9732
0.001052	1.0447	0.001034	1.0269	7.127E-4	1.0609	0.001173	0.9939
0.001286	1.0544	0.001245	1.0350	8.606E-4	1.0738	0.001245	0.9990
0.001410	1.0596	0.001389	1.0416	0.001913	1.1734	0.00239	1.0998
0.002337	1.0999	0.002527	1.0890	0.002888	1.2734	0.003314	1.1897
0.003258	1.1409	0.003600	1.1366	0.00365	1.3578	0.004602	1.3272
0.005318	1.2364	0.004699	1.1862	0.004898	1.5091	0.006079	1.5016
0.007149	1.3261	0.006397	1.2659	0.005922	1.6478	0.007351	1.6722
0.008797	1.4096	0.008051	1.3478	0.007348	1.8689	0.008592	1.8556
0.011459	1.5538	0.009684	1.4318				
0.013627	1.6770	0.012836	1.6027				
0.016246	1.8327	0.015683	1.7690				

regularly with increasing concentration. In the extremely dilute concentration region the η_r versus *C* plot exhibits good linearity as shown in Fig. 2. The intercept *A*, slope *B* and linear correlation coefficient *R* obtained by apparent linear fitting for the η_r data in the extremely dilute concentration region are listed in Table 2. The intercept is greater than one for the data measured in the original viscometer while it is less than one for the data measured in the paraffin-coated viscometer. However, the ratio of slope to intercept *B*/*A* is practically the same for both cases. This ratio may be regarded as an approximation to intrinsic viscosity. The fact that the linear regression line did not pass through the origin (0,1) indicates that there exist systematic errors due to wall effects with different causes for the two viscometers.

The differences between these two data sets are more pronounced in the reduced viscosity versus concentration plots as shown in Fig. 3. The reduced viscosity measured in the paraffin-coated viscometer turns downwards from the linear portion, while that measured in the original viscometer turns upwards with decreasing concentration in the

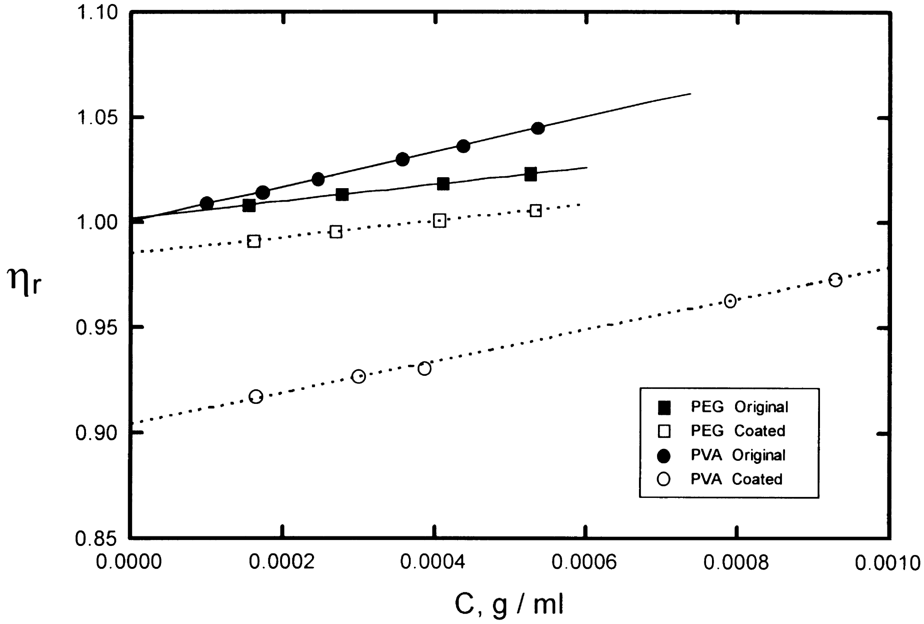

Fig. 2. Effect of capillary surface coating with paraffin on the relative viscosity of aqueous solution of PEG and PVA in the extremely dilute concentration region.

Table 2
Apparent linear fit to the relative viscosity versus concentration plot in the extremely dilute concentration region

Polymer	Viscometer	*A*	*B*	*R*	*B*/*A*	*A* − 1
Polyethylene glycol	Original	1.00195	39.78	0.9999	39.7	0.001954
	Paraffin coated	0.98503	38.60	0.9994	39.2	− 0.01497
Polyvinyl alcohol	Original	1.00037	82.96	0.9999	82.9	0.00037
	Paraffin coated	0.90408	73.98	0.9986	81.8	− 0.09592

extremely dilute concentration region. The cause of the upward inflection of the reduced viscosity versus concentration plot is the reduction of capillary radius due to the adsorption of polymer chains onto the inner wall surface of the viscometer capillary [16,17,3–5]. The effect of adsorption of polymer on the measured relative viscosity could be quantitatively expressed as [3–5]

$$\eta_{r,\mathrm{exp}} = \frac{t(C)}{t_0(0)} = \eta_{r,\mathrm{true}}\left(1 + \frac{kC}{C_\mathrm{a} + C}\right) \tag{5}$$

where $t(C)$ is the flow time of solution with given concentration C, C_a is a particular concentration at which half of the active sites of the viscometer wall are occupied by the adsorbed solute molecules. The parameter k in Eq. (5) accounts for the maximum fractional change of flow time of solvent due to solute adsorption defined as

$$k = \frac{t_0(1) - t_0(0)}{t_0(0)} \tag{6}$$

where $t_0(1)$ is the effective flow time of pure solvent as all of the active sites of the capillary wall surface are saturated with adsorbed solute molecules. The true relative viscosity of dilute polymer solutions can best be represented by [18]

$$\eta_{r,\mathrm{true}} = 1 + [\eta]C + 6K_m[\eta]C^2 \tag{7}$$

where K_m is the self-association constant of polymer in solution and is related to the conventional Huggins slope constant k_H as

$$K_m = \frac{k_\mathrm{H}[\eta]}{6}. \tag{8}$$

Then the experimental reduced viscosity will be

$$\frac{\eta_{sp}}{C} = \frac{k}{C_\mathrm{a} + C} + \left([\eta] + 6K_m[\eta]C\right)\left(1 + \frac{kC}{C_\mathrm{a} + C}\right) \tag{9}$$

in which the solute adsorption effect is taken into account.

Eqs. (5), (7), (9) could satisfactorily express the experimental viscosity data for aqueous PEG solution measured both in the original and paraffin-coated viscometers with the viscosity parameter $[\eta]$, K_m, k and C_a listed in Table 3. These parameters are obtained by iterative data fitting procedure to Eq. (9) with B/A and $A - 1$ as the initial guesses for $[\eta]$ and k. The calculated relative and reduced viscosity concentration dependence curves with these parameters well coincide with the experimental points as shown in Figs 1 and 3. The effective adsorbed layer thickness of polymer chain $b_\mathrm{adsorption}$ on the glass surface could be evaluated from parameter k by

$$b_\mathrm{adsorption} = R\left(1 - \frac{1}{(1 + k)^{1/4}}\right) \tag{10}$$

with the same reasoning as for b_coat in Eq. (4). The result obtained is listed in Table 4.

The experimental viscosity data for aqueous solutions measured in the paraffin-coated viscometer need a thorough discussion. Owing to the hydrophobic nature of paraffin, at first we expected that the adsorption of solute would not occur and the viscosity data should possess normal behavior, that is, yielding a linear reduced viscosity-concentration plot. The actual experimental data are inconsistent with this conjecture. However, Eqs. (5), (9) still satisfactorily fit the experimental data with a negative k and a zero C_a as shown in Figs 1 and 3. This suggests that another mode of wall effects operates in this case. The term $(1 + kC/(C_\mathrm{a} + C))$ in Eq. (5) may be regarded as a correction term for wall effects. Applying this correction to the relative viscosity measured in the original and paraffin-coated viscometer and listed in Table 1, the corrected reduced viscosity versus

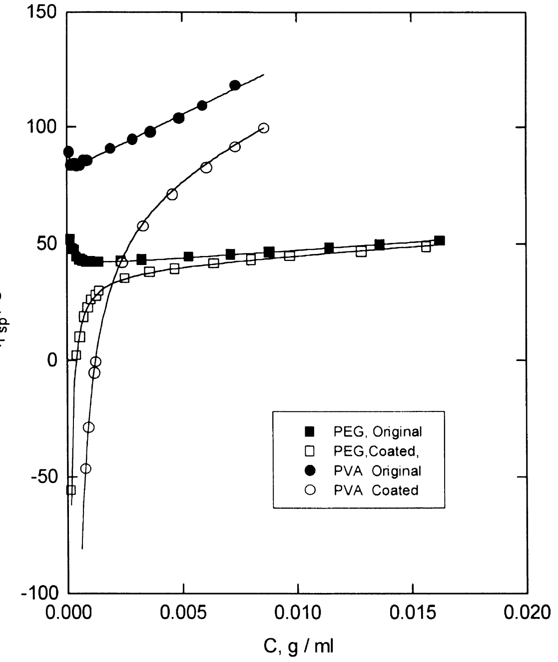

Fig. 3. Effect of capillary surface coating with paraffin on the reduced viscosity of aqueous solution of PEG and PVA.

Table 3
Viscosity parameters of aqueous solution of polyethylene glycol and polyvinyl alcohol obtained by fitting the reduced viscosities measured in original and paraffin coated viscometers to Eq. 9

Polymer	Viscometer	$[\eta]$ (ml/g)	K_m	k	C_a (g/ml)
Polyethylene glycol	Original	39.98	2.923	0.00186	3.97E-6
	Paraffin coated	39.98	2.923	− 0.01525	0
Polyvinyl alcohol	Original	80.62	10.15	0.00058	3.34E-7
	Paraffin coated	80.62	10.15	− 0.09592	0

concentration plots coincide with each other very well as shown in Fig. 4. This means that the wall effects are properly eliminated for both cases.

In the sense of solute adsorption, a negative k value means not only the capillary radius but also the surface properties of the glass are changed. A zero C_a fits the experimental data and indicates the absence of solute adsorption. In view of the fact that the paraffin coating alters the surface properties completely, the observed difference must be attributed to the transition of the mode of capillary flow, that is from viscous flow to slip flow.

The rheological analysis of tube flow [6–13] predicts that the slip flow rate Q_{slip} is faster than the viscous flow rate Q_{viscous} through the same tube as

$$Q_{\mathrm{slip}} = Q_{\mathrm{viscous}} + \pi R^2 v_s \tag{11}$$

where v_s is the slip-flow velocity of the fluid along the tube wall surface. Applying this prediction to water flow in the present case, at first sight it appears that the flow time of water in the paraffin-coated viscometer should be less than that in the original non-coated viscometer. If regarding $t_{0,\mathrm{coat}}(0)$ as the flow time of water in the slip flow mode and $t_{0,\mathrm{coat}}(1)$ calculated from parameter k by Eq. (6) as the flow time of water in viscous flow mode, the experimental fact seems contrary to this prediction. Therefore, seeking a more appropriate explanation is needed.

This extraordinary feature of slip flow of polymer solution down to the extremely dilute concentration region could be explained by the concept of extrapolation length b_{ex} of slip flow for polymer melts proposed by de Gennes [14,15]. The calculated flow time $t_{0,\mathrm{coat}}(1)$ corresponds to the flow time of water in a hypothetical capillary, its radius equal to $(R - b_{\mathrm{coat}} + b_{\mathrm{ex}})$ as shown schematically in Fig. 5.

According to de Gennes, the extrapolation length b_{ex} relates to the slip flow velocity of fluid v_s at the capillary wall surface as

$$b_{\mathrm{ex}} = \frac{v_s}{\gamma_w} \tag{12}$$

where γ_w is the shear rate at wall surface. The shear stress at wall surface is

$$\tau_w = \frac{R \cdot p}{2 \cdot L}. \tag{13}$$

From the definition of viscosity

$$\tau = \eta \cdot \gamma \tag{14}$$

we have

$$v_s = b_{\mathrm{ex}} \cdot \gamma_w = \frac{b_{\mathrm{ex}} \cdot R \cdot p}{2 \cdot L \cdot \eta}. \tag{15}$$

Using this quantity to calculate the volume slip flow rate of fluid

$$Q_{\mathrm{slip}} = \int_0^R 2 \cdot \pi \cdot r \cdot \left[\frac{p}{4 \cdot \eta \cdot L} \cdot (R^2 - r^2) + \frac{\mathbf{b}_{\mathrm{ex}} \cdot R \cdot p}{2 \cdot L \cdot \eta} \right] \cdot dr \tag{16}$$

after integration

$$Q_{\mathrm{slip}} = \frac{\pi p R^3}{8 \eta l} (R + 4 b_{\mathrm{ex}}) \tag{17}$$

or, alternatively, we have

$$Q_{\mathrm{slip}} = Q_{\mathrm{vis}} \cdot \left(1 + 4 \cdot \frac{b_{\mathrm{ex}}}{R} \right) \tag{17a}$$

which is similar to Eq. (11).

The slip velocity and extrapolation length may be varied from solvent to solution. Denoting the volume flow rate of solution as Eq. (17) and that of solvent as

$$Q_{\mathrm{slip},0} = \frac{\pi p R^3}{8 \eta_0 l} (R + 4 b_{\mathrm{ex},0}) \tag{18}$$

Table 4
The effective adsorbed layer thickness and slip flow extrapolation length of PEG and PVA deduced from viscosity data

Polymer	Viscometer	$t_0(0)$ (s)	$t_0(1)$ (s)	R (mm)	b_{coat} (mm)	b_{ads} (mm)	Δb_{ex} (mm)
Polyethylene glycol	Original	290.80	291.34	0.221	0	0. 000103	–
	Paraffin coated	313.56	308.86	0.221	0.004124	–	0.00084
Polyvinyl alcohol	Original	290.85	291.02	0.221	0	0.000032	–
	Paraffin coated	323.56	292.52	0.221	0.005811	–	0.0053

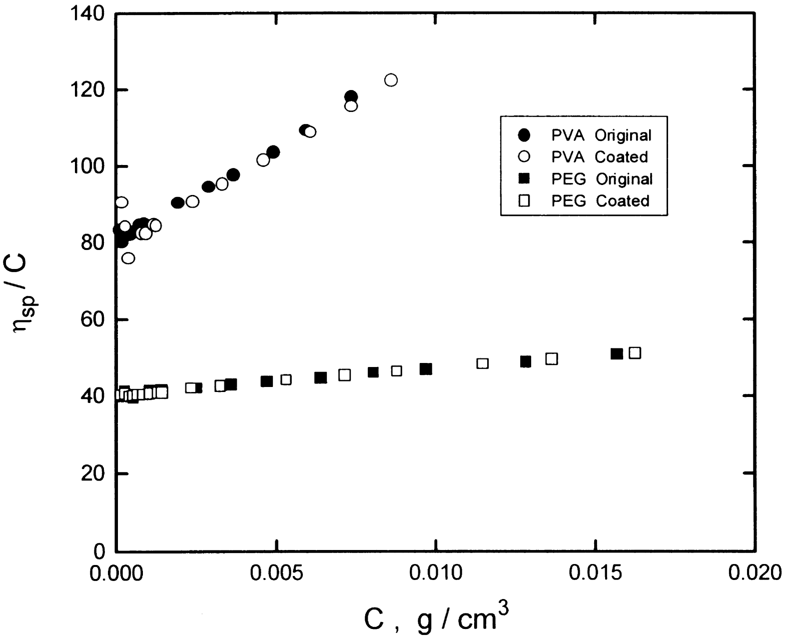

Fig. 4. The reduced viscosity versus concentration plot of PEG aqueous solution after wall-effect correction.

then the experimental relative viscosity

$$\eta_{r,\mathrm{exp}} = \frac{Q_{\mathrm{slip},0}}{Q_{\mathrm{slip}}} = \frac{\eta}{\eta_0}\,\frac{1+\dfrac{4b_{\mathrm{ex},0}}{R}}{1+\dfrac{4b_{\mathrm{ex}}}{R}}. \tag{19}$$

Denoting the difference between the extrapolation length of solution and that of solvent as

$$\Delta b_{\mathrm{ex}} = b_{\mathrm{ex}} - b_{\mathrm{ex},0} \tag{20}$$

then Eq. (19) could be simplified to

$$\eta_{r,\mathrm{exp}} = \eta_r\left(1 - 4\frac{\Delta b_{\mathrm{ex}}}{R}\right). \tag{21}$$

Eqs. (20), (21) predict that, as the extrapolation length of solution is longer than that of solvent, the experimental relative viscosity of solution will be smaller than the true value as in the situation we met here. Comparing Eq. (21) with Eq. (5) for $C_a = 0$

$$\eta_{r,\mathrm{exp}} = \frac{t(C)}{t_0(0)} = \eta_{r,\mathrm{true}}(1 + k) \tag{5a}$$

immediately we have

$$\Delta b_{\mathrm{ex}} = -\frac{kR}{4} \tag{22}$$

which indicates that the extrapolation length difference Δb_{ex} could be evaluated unambiguously from the negative k value and the radius of the viscometer capillary. All the calculated thickness, hypothetical flow time of water $t_0(1)$ resulting from parameter k and the experimental flow times of water $t_0(0)$ are listed together in Table 4 for ease of comparison. It should be noted that the adsorbed layer thickness of PVA onto the glass surface of the original viscometer is much thinner than that of PEG. This is probably because only the hydroxyl end group of the PEG chain is adsorbed on to the glass surface while the adsorbed PVA chain takes a flattened conformation. On the other hand, the extrapolation length difference of PVA solution is 6.5 times thicker than that of PEG solution in the paraffin-coated viscometer. This suggests that the repulsive force between the flowing PVA chain and the paraffin coating is stronger than that of PEG chains.

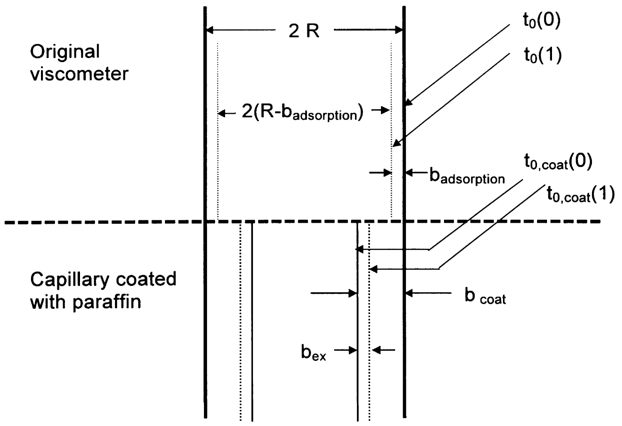

Fig. 5. Schematic representation of the capillary dimension and the flow time of water through a viscometer with and without paraffin coating.

4. Conclusions

From the preceding discussions the following conclusions were reached:

1. Modification of the glass surface of a viscometer capillary by paraffin coating leads to a transition of the mode of capillary flow of water from ordinary viscous flow to slip flow.
2. The formula proposed for describing the effect of solute adsorption on relative and reduced viscosity measured under viscous flow mode is also applicable to slip flow mode.
3. The lowering of the experimental relative viscosity of a solution in the slip flow mode could be explained by the concept of extrapolation length difference of solution and solvent proposed by de Gennes [14] which may be evaluated unambiguously from the negative parameter k of the wall effect correction term for the relative viscosity of polymer solutions.

Acknowledgements

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