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Effect of concentration reduction due to adsorption on the reduced viscosity of polymer solution in extremely dilute concentration regime

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Abstract

The phenomena of reduced viscosity bending up and sometimes appearing a maximum in extremely dilute concentration regime of polymer solution are resulted from the concentration reduction due to adsorption of polymer onto the glass capillary wall. A quantitative theoretical description of this effect based on Langmuir adsorption isotherm is given. Applying the deduced formula to fit Ohrn's precisely measured reduced viscosity data of polystyrene, linear and branched polyvinyl acetate solutions for three viscometers with different capillary radius gave satisfactory results. The radius dependence of the effective adsorption layer thickness of these polymers indicates it consists of two parts, that is a true adsorption layer and a repulsion layer between anchored chains on the capillary surface and flowing chains in solution. The reduced viscosities of an ultrahigh molar mass polyethylene oxide sample in aqueous solution were measured both by an ordinary glass viscometer and by a viscometer constructed with a polytetrafluoroethylene capillary. The former exhibits a maximum due to adsorption and the later possesses the typical behavior of slipping flow. After correction for solute adsorption and slippage, respectively, the two sets of data coincide well and gave a common linear reduced viscosity plot down to extremely dilute concentration regime.

Keywords: Concentration reduction; Polymer adsorption; Adsorption layer thickness

1. Introduction

Adsorption of polymer chains onto other heterogeneous substrates has all along been an important research issue whether in theoretical respect [1–4] or in practical applications, such as polymer cushions between the lipid layer and solid substrate [5], water treatment as flocculating/water insoluble mixtures [3,4], powder processing as dispersion agents [6], etc. Glass is a material, familiar and easily obtained, and has been widely used as a substrate for research purposes [7,8]. Whereas, viscometer usually used as a tool for viscosity measurement is made of glass materials and unavoidably subjected to adsorption of polymer chains during viscosity measurement, which disturbs the availability of the true information of polymer chains in solution. Recently great attention has been paid to the viscosity anomalies of polymer solution down to the extremely dilute concentration region [9–18]. These experimental results [19–27] proves that the adsorption of polymer chain onto glass capillary surface leads to the up-bending of reduced viscosity versus concentration plot occurred in the extremely dilute concentration regime due to existence of hydroxyl group on the glass surface. For describing such interfacial phenomena, the present authors have developed a quantitative expression which could successfully explain the up-bending and down-bending curves at the extremely dilute concentration [2,3,8–10]. However, the expression could not, as a matter of fact, explain why there sometimes appeared the viscosity maximum at the extremely dilute concentration regime. Batzer [19], and Ohrn [22,23] have observed such reduced viscosity maximum but the reasons of their appearance keep unsolved yet.

Obviously, in the extremely dilute concentration region once the polymer chains were adsorbed onto the glass capillary

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surface, the equilibrium concentration should be diminished as compared with the initial nominal concentration. In the present paper, the effect of concentration reduction due to adsorption on the reduced viscosity of polymer solution in extremely dilute concentration regime will be analyzed quantitatively based on Langmuir adsorption isotherm. A formula accounted for concentration reduction due to polymer adsorption has been deduced and performed to solve the problem of viscosity maximum by revisiting Ohrn's data of toluene solutions of polystyrene, linear and branched polyvinyl acetate measured by a viscometer constructed with three capillaries of different radius. Since the viscosity maximum never appears in the case of slipping flow, for verifying the present theoretical predictions, we also carried out an experiment to measure the viscosity of an aqueous solution of a polyethylene oxide sample with high molar mass in viscometer constructed with a polytetrafluoroethylene (PTFE) compared with that in a common glass viscometer and applying the concentration reduction correction to both cases.

2. Experimental

2.1. Samples

The PEO sample with a high molar mass was kindly provided by Prof Jiang in Changchun Institute of Applied Chemistry, Chinese Academy of Sciences.

2.2. Viscometers

The glass capillary part of an Ubbelohde type viscometer was displaced by a Teflon capillary using a special method [17]. The inner diameter of the PTFE capillary was measured to be 0.573 mm. A conventional glass viscometer with a capillary of 0.40 mm diameter was also used to measure the viscosity of the same solution. It is important to clean both viscometers carefully as described in previous papers [17,18]. For cleaning the glass viscometer, first to soak it in a chromic acid mixture for a day, then to rinse the viscometer repeatedly with deionised distilled water, and finally to rinse it with boiled deionized distilled water under ultrasonic vibrations. At last the clean glass viscometer was sent to a common oven to dry at 125 °C. For cleaning PTFE capillary viscometer, except the step of soaking in chromic acid mixture was omitted, the other procedures were the same as for cleaning the glass viscometer. The thoroughly cleaned PTFE capillary viscometer was sent to a vacuum oven to dry at 85 °C.

2.3. Viscosity measurements

An aqueous stock solution of the polyethylene oxide sample were freshly prepared by weighing and then filtered through a sintered G5 filter to remove the dust. The viscosity measurements were performed at 30±0.05 °C. According to the sequence from low to high concentration, a known weight of pure solvent (water) was first transferred into the viscometer and its efflux time was measured. The constancy of the solvent efflux time serves as a criterion for judging the cleanness of the viscometer and the consistency of the experimental conditions. The efflux times of water in the glass and PTFE capillary viscometers at 30 °C are 233.95 and 158.69 s, respectively.

After the efflux time of the solvent was measured, a definite amount of stock sample solution with a known weight concentration was added into the viscometer by weighing and then a syringe was used to produce air purge to mix the solution well in the viscometer. After about half an hour the efflux time of the solution was measured. This operation was repeated successively until the relative viscosity reaches a predetermined point. To examine whether the solution was mixed well, it can be judged by the constancy of the flow time of the measured solution. The ratio of the efflux time of the solution, t_{solu}, to that of solvent, t_{solv}, was regarded as the experimental relative viscosity, $\eta_{\mathrm{r}}=t_{\mathrm{solu}}/t_{\mathrm{solv}}$. The obtained weight concentration of the solution in g/g was converted to weight–volume concentration in g/ml by applying density correction.

3. Results and discussion

3.1. Theoretical background

The experimental relative viscosity of a polymer solution is usually calculated according to [10,11]

$$\eta_{\mathrm{r,exp}}=\frac{t(C_0)}{t_0} \tag{1}$$

where $t(C_0)$ and t_0 are the flow time of the solution with a definite concentration C_0 and the flow time of pure solvent in a given viscometer, respectively. Owing to the existence of interfacial interactions between flowing solution and capillary wall surface, a correction factor exists to correlate the true and the experimental relative viscosity as

$$\eta_{\mathrm{r,exp}}=f_{\mathrm{int}}\eta_{\mathrm{r,true}} \tag{2}$$

The correction factor f_{int} had been derived by one of the present authors [10] as

$$f_{\mathrm{int}}=\left(1+\frac{kC_0}{C_{\mathrm{a}}+C_0}\right) \tag{3}$$

where k is a constant which characterizes the interfacial interactions on the flow time of solvent and C_{a} is a characteristic concentration at which the surface coverage of the adsorbed polymer equals to 1/2. A positive k means the polymer will anchor on the capillary wall surface and results in an up-bending reduced viscosity versus concentration plot with $C_{\mathrm{a}}>0$. A negative k with $C_{\mathrm{a}}=0$ indicates the flow mode of the solution has been converted from viscous to slipping and results in a down-bending reduced viscosity versus concentration plot. In the case of polymer adsorption, an effective adsorbed layer thickness b_{eff} could be deduced from parameter k as

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

where R is the radius of the capillary.

Based on the assumptions that Einstein viscosity law is valid for non-associable dilute polymer solution

$$\eta_{\mathrm{r}} = 1 + [\eta]C_0 \tag{5}$$

and any deviation from it is due to macromolecular self-association or cluster formation, the true relative viscosity of polymer solution may be represented by [12,13]

$$\eta_{\mathrm{r,true}} = 1 + [\eta]C_0 + 6K_{\mathrm{m}}[\eta]C_0^2 \tag{6}$$

where K_{m} is self-association constant of polymer chains in solution and numerically correlates with the Huggins coefficient k_{H} and intrinsic viscosity $[\eta]$ as [10]

$$K_{\mathrm{m}} = \frac{k_{\mathrm{H}}[\eta]}{6} \tag{7}$$

Combining Eqs. (2), (3) and (6), the experimental relative viscosity of polymer solution should be expressed as

$$\eta_{\mathrm{r,exp}} = \left(1 + [\eta]C_0 + 6K_{\mathrm{m}}[\eta]C_0^2\right)\left(1 + \frac{kC_0}{C_{\mathrm{a}} + C_0}\right) \tag{8}$$

Consequently, the experimental reduced viscosity will be

$$\frac{\eta_{\mathrm{sp}}}{C_0} = \frac{\left(1 + [\eta]C_0 + 6K_{\mathrm{m}}[\eta]C_0^2\right)\left(1 + ((kC_0)/(C_{\mathrm{a}} + C_0))\right) - 1}{C_0} \tag{9}$$

Expanding Eq. (9) we have

$$\frac{\eta_{\mathrm{sp}}}{C_0} = \frac{k}{C_{\mathrm{a}} + C_0} + [\eta](1 + 6K_{\mathrm{m}}C_0)\left(1 + \frac{kC_0}{C_{\mathrm{a}} + C_0}\right) \tag{10}$$

Eq. (10) shows that if the effect of concentration reduction due to solute adsorption is neglected, the experimental reduced viscosity versus concentration plot will bend up in extremely dilute concentration regime and tend to a limiting value k/C_{a} as C_0 approaches to zero.

3.2. Concentration reduction

Placing V (ml) polymer solution with initial concentration C_0 into a glass viscometer, the equilibrium concentration C of the solution should be diminished due to solute adsorption onto the wall surface of the viscometer. Denoting the maximum amount of polymer adsorbed per unit area on glass by $G_{\max}$ in unit g/cm^2, according to Langmuir adsorption isotherm the fractional coverage of the glass surface in contact with solution due to adsorption should be expressed as

$$\theta = \frac{G(C)}{G_{\max}} = \frac{bC}{1 + bC} = \frac{C}{C_{\mathrm{a}} + C} \tag{11}$$

where $G(C)$ is the specific solute adsorption amount at equilibrium concentration C and the characteristic concentration $C_{\mathrm{a}} = 1/b$ have the same physical meaning cited above. Therefore, the absolute solute adsorption amount $W_{\mathrm{a}}(C)$ at equilibrium concentration C is

$$W_{\mathrm{a}}(C) = \frac{SG_{\max}C}{C_{\mathrm{a}} + C} \tag{12}$$

where S is the contacting area of solution with the viscometer. Owing to the solute amount W in initial solution is

$$W = C_0 V \tag{13}$$

then the concentration C at adsorption equilibrium becomes

$$C = \frac{[W - W_{\mathrm{a}}(C)]}{V} = C_0\left[1 - \left(\frac{SG_{\max}}{V}\right)\left(\frac{C}{C_0(C_{\mathrm{a}} + C)}\right)\right] \tag{14}$$

Defining

$$A = \frac{SG_{\max}}{V} \tag{15}$$

and disregarding the small difference between C and C_0 for the correction term in the bracket of Eq. (14), we have the expression of the actual equilibrium concentration as

$$C = C_0\left(1 - \frac{A}{(C_{\mathrm{a}} + C_0)}\right) \tag{16}$$

The fractional reduction in concentration, therefore, is

$$\frac{(C_0 - C)}{C_0} = \frac{A}{(C_{\mathrm{a}} + C_0)} \tag{17}$$

which is determined by the relative magnitudes of C_{a} and A, and in turn both of them are depending on the ability and capacity of adsorption on glass surface. As $C_0 = C_{\mathrm{a}}$, the equilibrium concentration becomes

$$C_{C_0 = C_{\mathrm{a}}} = C_{\mathrm{a}} - \frac{A}{2} \tag{18}$$

which is useful to locate the position of C_{a} and to estimate the magnitude of parameter A.

3.3. Reduced viscosity maximum

Inserting the equilibrium concentration of Eq. (16) into Eq. (9) instead of the initial concentration originally presented in the equation, we have the final expression of the experimental reduced viscosity as

$$\frac{\eta_{\mathrm{sp}}}{C_0} = \frac{\left[1 + [\eta]C_0\left(1 - \frac{A}{C_{\mathrm{a}}+C_0}\right) + 6K_{\mathrm{m}}[\eta]\left[C_0\left(1 - \frac{A}{C_{\mathrm{a}}+C_0}\right)\right]^2\right]\left[1 + k\frac{C_0\left(1 - \frac{A}{C_{\mathrm{a}}+C_0}\right)}{C_{\mathrm{a}} + C_0\left(1 - \frac{A}{C_{\mathrm{a}}+C_0}\right)}\right] - 1}{C_0} \tag{19}$$

The experimental reduced viscosities are generated from two different sources. The first source is the true relative viscosity of polymer solution itself as described by the first bracket of the numerator of Eq. (19) or briefly by Eq. (6). The second source is raised from the interfacial effect during measuring viscosity as described in the second bracket of the numerator or by notation

$$f_{\mathrm{int}} = 1 + k\frac{C_0(1-(A/(C_{\mathrm{a}}+C_0)))}{C_{\mathrm{a}}+C_0[1-(A/(C_{\mathrm{a}}+C_0))]} \qquad (20)$$

Thus, Eq. (19) may be shortened to the general form

$$\frac{\eta_{\mathrm{sp}}}{C_0} = \frac{\eta_{\mathrm{r,true}} f_{\mathrm{int}} - 1}{C_0} \qquad (21)$$

Generally $\eta_{\mathrm{r,true}}$ is a monotonically increasing function of concentration. The reduction of concentration modifies f_{int} from Eqs. (3) to (20) and causes the appearance of a maximum in the reduced viscosity versus concentration plots as illustrated by Figs. 1 and 2. Fig. 1 using Eq. (19) numerically simulates the general behavior of a neutral polymer with a low k of 0.002 and varying A. Fig. 2 simulates the behavior of a polymer with a higher k of 0.100 and $K_{\mathrm{m}}=0$, i.e. the polymer has a higher tendency to be adsorbed but the inter-chain self-association being avoided due to the existence of inter-chain repulsive forces.

Figs. 1 and 2 indicate that the reduced viscosity maximum locates in the extremely dilute concentration regime. In this regime, $\eta_{\mathrm{r,true}}$ takes a value near one and contributes nothing to the appearance of viscosity maximum of reduced viscosity versus concentration plot. The occurrence of a maximum solely attributes to f_{int}. Taking the derivative $(\mathrm{d}/\mathrm{d}C_0)((f_{\mathrm{int}}-1)/C_0)$ and letting it equal zero, we obtained the concentration at reduced viscosity maximum $C_{\max}$ as

$$C_{\max} = A - C_{\mathrm{a}} + \sqrt{AC_{\mathrm{a}}} \qquad (22)$$

The estimated $C_{\max}$ values by Eq. (22) well coincide with the actual values as shown in Figs. 1 and 2.

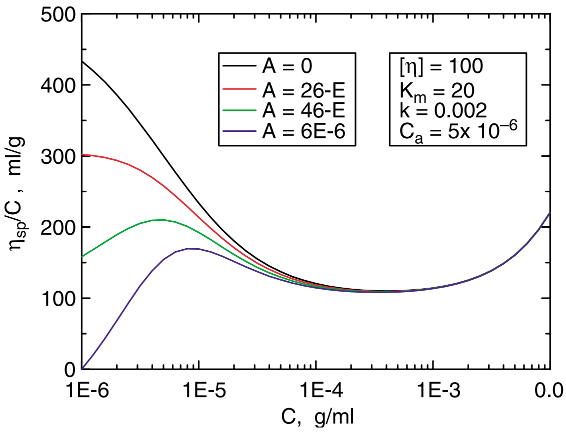

Fig. 1. Simulated reduced viscosity versus concentration plots for polymer solutions with K_{m} greater than zero.

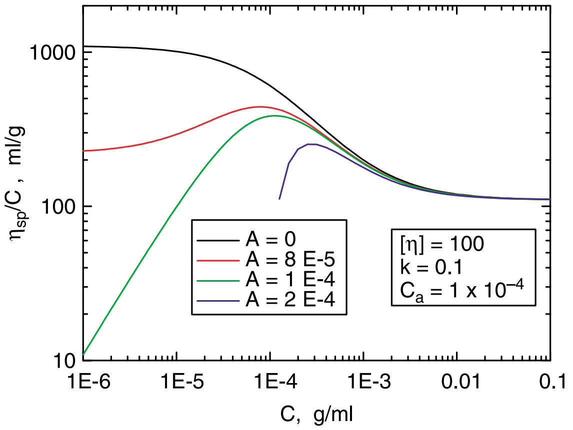

Fig. 2. Simulated reduced viscosity versus concentration plots for polymer solutions with K_{m} equal to zero.

3.4. Revisit Ohrn's results

More than 40 years ago, Öhrn [22,23] established the concept of polymer adsorption will diminish the radius of capillary in viscometry and lead to an upward curvature in the extremely dilute concentration regime of reduced viscosity plot. The correctness of this concept was verified by performing precision solution viscosity measurements using a specially constructed viscometer consisting of three capillaries with different diameters. He studied the toluene solution of three polymers, namely polystyrene, linear polyvinyl acetate and branched polyvinyl acetate. The reduced viscosity plots of all these samples are up-bending and the degree of the upward curvature decrease with increasing capillary diameter as the conceptual theory predicts. However, for the last two polymer samples, distinct reduced viscosity maximums occurred in extremely dilute regimes. The reasons of the appearing maximum remains unsolved yet. In the present article, we try to solve the problem first by revisiting his experimental data.

The dimension of the viscometer designed by Ohrn is replicated in Table 1, in which the contact surface area S is estimated as the sum of inner wall surface area of capillary and measuring bulb assuming the later is spherical.

He gave the original viscosity data of polystyrene in detail, but for the other two polymers only gave the diagrams of reduced viscosity versus concentration plots. We first digitized the diagrams by using a data-digitizer software WinDIG and then re-plotted them as shown in Figs. 3–5 for polystyrene, linear and branched polyvinyl acetate, respectively. Afterwards the diagrams were used to fit Eq. (19) by non-linear curve fit function of software ORIGIN. The fitted curves are also drawn in these figures. The fitted curves are consonant with

Table 1
The dimension of Ohrn viscometer

Viscometer capillary	Bulb volume (ml)	Capillary length (cm)	Capillary radius (mm)	Surface area (cm^2)
S1	25	40	0.25	47.6
S2	10	24	0.15	24.7
S3	3	17	0.1	11.1

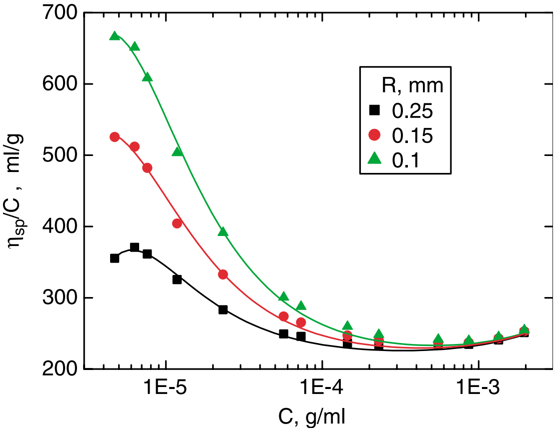

Fig. 3. Variation of reduced viscosity with concentration of toluene solution of linear polystyrene measured by a viscometer constructed with three capillaries reported by Ohrn [22]. The solid curves are the calculated curves by Eq. (19) with parameters listed in Table 2.

experimental data quite well. Thus we could evidently conclude that the occurrence of reduced viscosity maximum in extremely dilute regime is eventually caused by concentration reduction due to polymer adsorption onto capillary wall surface.

The viscosity parameters of the fitted curves in Eq. (19) obtained by ORIGIN are listed in Table 2 for the three samples measured with three different capillaries. Inspecting the data in Table 2, several interesting features will be reached.

First of all, the K_m value of branched polyvinyl acetate is much more higher than that of linear polymer though its intrinsic viscosity [η] is lower. This feature is in accordance with the theoretical prediction made by Pan and Cheng [14,28, 29].

Secondary, the parameter k is defined as the fractional increment of flow time of solvent through the capillary saturated with adsorbed polymer compared with that of solvent through the clean bare capillary, and is a measure of the ability of the polymer adsorption by which an effective adsorbed layer thickness could be evaluated as described by Eq. (4). The magnitude of k depends on the radius of capillary. A plot of k versus reciprocal of capillary radius yields a straight line with a small but definite intercept at $1/R=0$, as shown in Fig. 6. That is to say the expression

$$k = k_0 + \frac{\beta}{R} \tag{23}$$

is adequate to describe the capillary dimension dependency of parameter k. The value of k_0 was marked in Fig. 6. It clearly indicates that the effective adsorption layer thickness b_{eff} derived from k by Eq. (4) is built up by two parts, one is the actual adsorption layer anchored on the capillary wall surface and the other is an exclusion or repulsion layer between the flowing and anchored polymers raised from inter-chain repulsive interactions. By notation, we may write

$$b_{\mathrm{eff}} = b_{\mathrm{rep}} + b_{\mathrm{ads}} \tag{24}$$

where b_{ads} denotes the actual adsorption layer thickness and b_{rep} denotes the exclusion or repulsion layer thickness. Hence, b_{ads} may be evaluated by

$$b_{\mathrm{ads}} = R\left(1 - \frac{1}{(1+k-k_0)^{1/4}}\right) \tag{25}$$

and b_{rep} by the difference

$$b_{\mathrm{rep}} = b_{\mathrm{eff}} - b_{\mathrm{ads}} \tag{26}$$

The various adsorption layer thickness obtained are listed in Table 3. The data in the table illustrates that:

(1) The actual adsorption layer thickness b_{ads} is a constant for a given polymer and is independent on the dimension of capillary.

(2) The repulsion layer is compressible, its thickness b_{rep} increases with increasing radius of capillary for a given polymer as shown in Fig. 7. It gave a limiting value $b_{\mathrm{rep}}^{\infty}$ as the radius approaches to infinity, i.e. as $(1/R)$ approaches to zero. And as the capillary radius R becomes very small, the repulsion layer approaches to zero.

(3) For neutral polymers, the repulsion layer thickness is much lower than that of actual adsorption layer. The ratio of b_{ads} to $b_{\mathrm{rep}}^{\infty}$ lies within 7–11 for the three polymers.

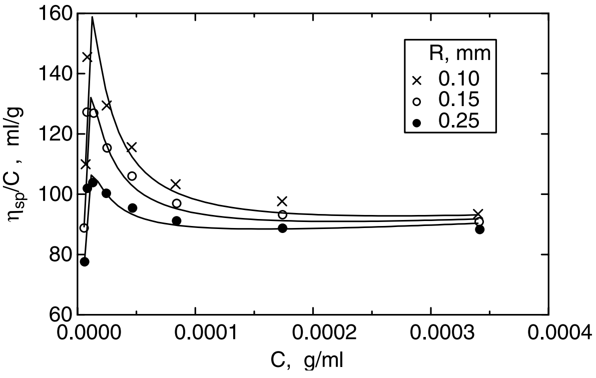

Fig. 4. Reduced viscosity curves of linear polyvinyl acetate in toluene measured by different capillaries obtained by Ohrn [22]. The solid curves are the calculated curves by Eq. (19) with parameters listed in Table 2.

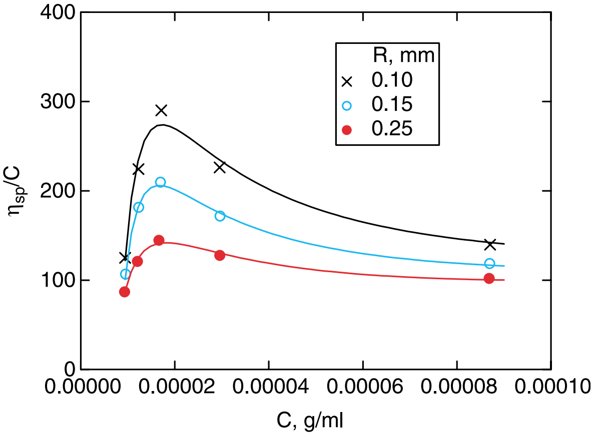

Fig. 5. Reduced viscosity curves of branched polyvinyl acetate in toluene measured by different capillaries obtained by Ohrn [22]. The solid curves are the calculated curves by Eq. (19) with parameters listed in Table 2.

Table 2
Viscosity parameters obtained by fitting Ohrn's original data with Eq. (19)

Polymer	Capillary	[η], (ml/g)	K_m	k	$C_a\times 10^6$	$A\times 10^6$	$G_{max}\times 10^6$	
							Calculated	Experimental
Polystyrene	S1	214.6	12.9	0.00266	2.26	4.01	4.8	Not observed
	S2	214.6	12.9	0.00378	2.69	3.12	3.3	Not observed
	S3	214.6	12.9	0.00540	2.63	3.47	3.9	6.1
Linear PVAc	S1	82.3	40.0	0.00108	3.03	6.87	8.4	11.3
	S2	82.3	40.0	0.00158	3.24	7.07	8.6	10.6
	S3	82.3	40.0	0.00208	2.38	7.74	9.7	10.6
Branched PVAc	S1	51.23	828.3	0.00378	6.57	10	11.5	15.4
	S2	51.23	828.3	0.00515	4.60	10	12.2	16.0
	S3	51.23	828.3	0.00761	5.29	10	12.0	17.4

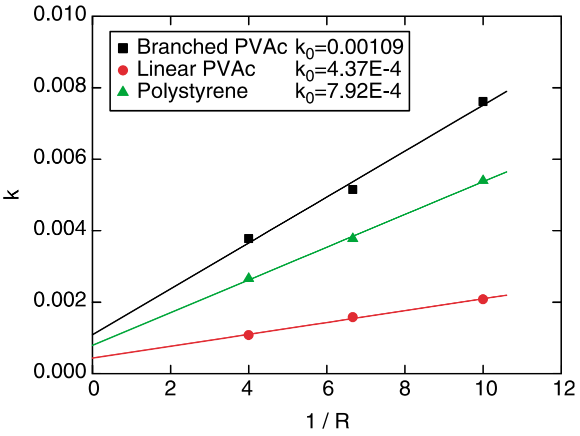

Fig. 6. Variation of parameter k with the reciprocal of capillary radius for various polymers.

Thirdly, the parameter C_a and A are physically mutual related, both of them reflect the capacity of adsorption and depend on the coverage and contacting surface of the viscometer with polymer solution. Hence, the dimension of the viscometer capillary, measuring and reservoir bulb, volume of solution used, the saturation amount of adsorption and so on all are influenced on the magnitude of these two parameters. In addition they are regarded as adjustable parameters in the data fitting process. For checking the credibility of these two parameters, a possible route is to compare the experimentally observed location of the reduced viscosity maximum with the calculated value from these two parameters by Eq. (22). From Table 2 it could be seen that the experimental C_{max} and theoretically estimated value from A and C_a (Eq. (22)) lying in the same degree of magnitude of concentration, is basically consistent. The small discrepancy is probably due to there is no restraint for the two mutual adjustable parameters in the data fitting process.

Figs. 8 and 9 reflects the change of both C_a and A with contacting area S, respectively. Comparing branched PVAc, linear PVAc and linear PS, interestingly whether C_a or A, the sequence of the magnitude of the three samples for the same capillary radius is branched PVAc > linear PVAc > linear PS. For the same radius capillary viscometer, the contacting area and solution volume should be the same. According to Eq. (15), this means that the sequence of the maximum amount of adsorption of the three samples is the same above. This is to say, branched PVAc is more easily to be adsorbed onto the glass surface than the linear PS, the linear PVAc has the mediated adsorption capacity.

3.5. Effect of slippage

According to the theoretical predictions cited above, a reduced viscosity maximum should necessarily occur in a sufficiently low concentration if and only if the adsorption onto capillary wall surface takes place. Sometimes we did not observe the appearance of a maximum as in the case of polystyrene shown in Fig. 3, the only reason is the experimental concentration did not extended to such a low value. On the other hand, if the flow mode of flowing solution is slipping rather than viscous, a down-bending reduced viscosity curve without any maximum should appear. For verifying these decisions, we measured the solution viscosity of a polyethylene oxide sample with ultrahigh molar mass in water by using an

Table 3
The adsorption layer thickness derived from viscosity data

Polymer	Capillary	b_{eff} (nm)	b_{rep} (nm)	b_{ads} (nm)	b_{rep} ($1/R=0$) (nm)	$\langle b_{ads}\rangle$ (nm)
Polystyrene	S1	166.0	49.5	116.5	66.4	114.3
	S2	141.4	29.7	111.7		
	S3	134.5	19.8	114.7		
Linear PVAc	S1	67.5	27.3	40.2	36.6	41.3
	S2	59.2	16.3	42.8		
	S3	51.9	10.9	41.0		
Branched PVAc	S1	235.7	68.1	167.0	91.2	160.2
	S2	192.5	40.8	151.7		
	S3	189.4	27.2	162.0		

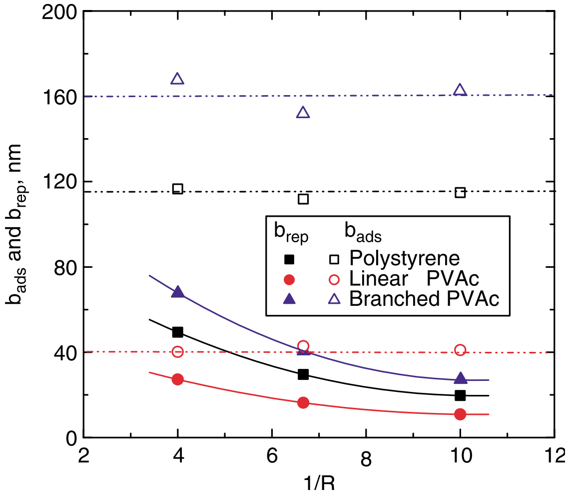

Fig. 7. Variation of the repulsion layer thickness b_{rep} and adsorption layer thickness b_{ads} with the reciprocal of capillary radius for various polymers.

ordinary glass viscometer and a viscometer constructed with a PTFE capillary.

The experimental reduced viscosity versus concentration plot for the glass viscometer was shown in Fig. 10. A maximum really exists in extremely dilute concentration regime. Applying Eq. (19) to fit the experimental data by mathematical software ORIGIN, the fitted curve coincides the experimental data quite well as shown in the figure. The concentration at which occurring a maximum estimated by Eq. (22) was also indicated in Fig. 10. The fitted parameters given by the non-linear curve fitting function of ORIGIN are. $[\eta]=7686$, $K_{\mathrm{m}}=686$, $k=0.0071$, $C_{\mathrm{a}}=4.50\times10^{-7}$, and $A=3.89\times10^{-7}$.

The effective adsorption layer thickness evaluated from parameter k is 453 nm. According to the Mark–Houwink equation suggested by Bailey and Kucern [30] for PEO in water and the relationship between intrinsic viscosity and radius of gyration suggested by Flory [31], the radius of gyration of this PEO sample in water is 390 nm. The adsorbed layer thickness of the polymer is lower than the coil diameter but somewhat greater than the corresponding radius of gyration, this fact indicates that the conformation of the adsorbed polyethylene oxide chain become slightly flattened compared with the sizes of coil in solution.

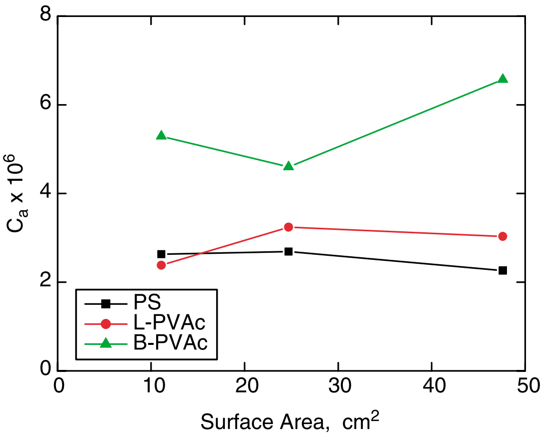

Fig. 8. Variation of characteristic concentration C_{a} with contacting area of polymer solution with viscometer inner surfaces.

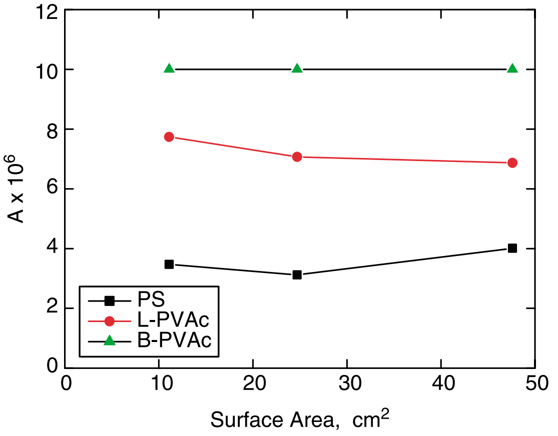

Fig. 9. Variation of concentration correction parameter A with contacting area of polymer solution with viscometer inner surfaces.

For eliminating adsorption effect during viscosity measurements in the glass viscometer, we measured the PEO aqueous solution in a PTFE capillary viscometer, which has been described in a previous paper [11]. In such a viscometer, slippage occurs for aqueous system instead of viscous flow as in the case of a paraffin-coated capillary viscometer [17]. As expected, in the PTFE viscometer the reduced viscosity versus concentration plot show a smoothly bent down curve without any indication of the appearance of a maximum in the same concentration range as shown in Fig. 11. Putting $[\eta]=7686$, $K_{\mathrm{m}}=686$, $C_{\mathrm{a}}=0$, and $A=0$, we get $k=-0.0255$, by using Eq. (19) to fit the experimental data. The negative sign of k means that slippage did occur [11]. By the definition of the correction factor of experimental relative viscosity for the interfacial effect, in the case of slipping flow, we have

$$f_{\mathrm{slippage}}=1+k \tag{27}$$

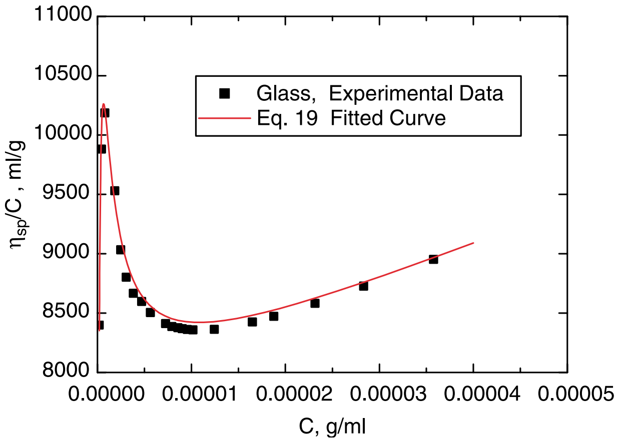

Fig. 10. Plots of reduced viscosity versus concentration for polyethylene oxide aqueous solution flowing in a glass capillary viscometer at 30 °C. Solid line is the calculated curve.

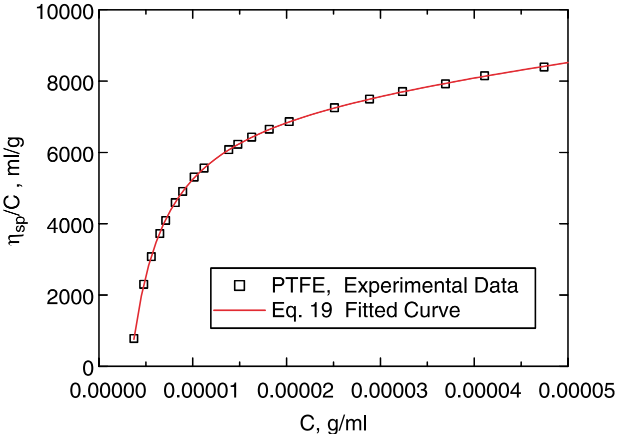

Fig. 11. Plots of reduced viscosity versus concentration for polyethylene oxide aqueous solution flowing in a polytetrafluoroethylene capillary viscometer at 30 °C. Solid line is the calculated curve.

and in the case of polymer adsorption

$$f_{\text{adsorption}} = \left[1 + k\frac{C_0(1-(A/(C_a + C_0)))}{C_a + C_0[1-(A/(C_a + C_0))]}\right] \tag{28}$$

Substituting Eqs. (27) and (28) into Eq. (2), we have the true relative viscosity of polymer solution

$$\eta_{r,\text{true}} = \frac{\eta_{r,\text{exp}}}{f_{\text{int}}} \tag{29}$$

According to the definition, the true reduced viscosity is the ratio of true specific viscosity to the true concentration. The true concentration could be represented by Eq. (16).

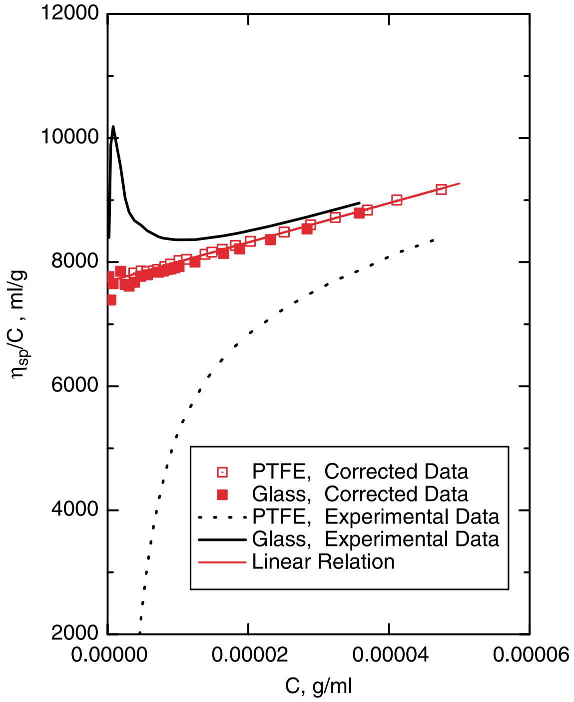

Fig. 12. Coincidence of corrected reduced viscosities of aqueous polyethylene oxide solutions with different flow modes.

Therefore, the following formula

$$\left(\frac{\eta_{sp}}{C}\right)_{\text{true}} = \frac{((\eta_{r,\text{exp}}/f_{\text{int}}) - 1)/(1-(A/(C_a + C_0)))}{C_0} \tag{30}$$

could be regarded as the corrected reduced viscosity. The corrected reduced viscosity versus concentration plots thus obtained for the two viscometers with different flow modes coincide with each other in one straight line as shown in Fig. 12. It indicates that the interfacial phenomenon is the most important source of abnormality in viscometry of polymer solution. By applying proper corrections as cited above, all these abnormalities could be eliminated.

4. Conclusions

Interfacial phenomenon between capillary surface and flowing solution is a common event met in usual viscosity measurement, which often leads to viscosity anomalies especially in the extremely dilute concentration regime. The interfacial phenomena are non-avoidable and are classified into two types. The first category is the adsorption of polymer onto capillary wall surface usually occurred in glass viscometers. It leads to the reduction of capillary diameter and the equilibrium concentration in the viscometer. These two simultaneously occurred effects could be quantitatively treated and expressed by a single simple formula. The viscosity abnormalities such as bending up and appearing a maximum in the extremely dilute concentration regime of the experimental reduced viscosity versus concentration plot are brought by polymer adsorption. Studying the capillary radius dependency of these abnormalities in extremely dilute solutions by viscosity measurement, knowledge about conformations and interactions of the adsorbed polymer could be obtained. The non-wetting of the solvent to the capillary surface leads to the second type of interfacial phenomenon. In the case slipping flow of the solution takes place instead of viscous flow. The reduced viscosity versus concentration plot shows a downward curvature monotonically with decreasing concentration. The both types of interfacial phenomena could be expressed by formula with similar form but different sign of the parameter involved. Using the deduced formula the experimental data could be corrected to eliminate the interference of the abnormalities.

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