

EFFECT OF ADSORPTION ON THE VISCOSITY OF DILUTE POLYMER SOLUTION*

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Abstract Careful measurements of the dilute solution viscosities of polyethylene glycol and polyvinyl alcohol in water were carried out. The reduced viscosities of both polymer solutions plot upward curves at extremely dilute concentration levels similar to the phenomena observed for many polymer solutions in the early 1950's. Upon observation of the changes of the flow times of pure water in and the wall surface wettability of the viscometer after measuring solution viscosity, a view was formed that the observed viscosity abnormality at extremely dilute concentration regions is solely due to the effect of adsorption of polymer chains onto the wall surface of viscometer. A theory of adsorption effect based on the Langmuir isotherms was proposed and a mathematical analysis for data treatment was performed. The theory could adequately describe the existing viscosity data. It seems necessary to correct the viscosity result of dilute polymer solutions measured by glass capillary viscometer by taking into account the effect of adsorption in all cases.

Keywords Adsorption, Polymer solution, Solution viscosity

INTRODUCTION

The viscosity of polymer solutions of extremely dilute concentration regions usually reveal some abnormalities. For instance, a graph of reduced viscosity plotted against concentration show either an upward or a downward curve as the concentration dips below a certain level. These unexpected facts have attracted the interest of many investigators since early 1950's^[1~16, 24, 25]. Most of them attempted to relate the concentration at which the graph curves to the critical concentration at which the physical contact of the polymer coil starts. However, others argued against this as the relative viscosity of an extremely dilute solution is very close to unity, and thus a high accuracy would be needed for the measurement^[17, 28]. Furthermore, a reduction in the radius of the viscometer capillary and the actual concentration of solution due to adsorption of the polymer from the solution may also influence the result^[19, 20, 21]. Though the most probable reason for the existence of abnormality is the hypothesis of adsorption, a quantitative explanation is still lacking.

All experimentalists who have been involved in measuring the viscosity of polymer solutions will know that the viscometer should be thoroughly cleaned after use in order to eliminate the influence of adhered polymer residues on the wall of the viscometer. In a recent viscometric study on dilute solutions of water soluble polymers, we noticed that after use the viscometer should be

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cleaned using boiling water. If the viscometer was cleaned only through repeated soaking and rinsing with water at ambient temperatures, the flow time of water increased nearly one percent as compared with that of a thoroughly cleaned viscometer. The wettability of the viscometer wall to water was also changed. These facts indicate that the polymer chains are quite firmly adsorbed onto the surface of viscometer wall and the flow time of the solvent would vary with the presence of an adsorbed polymer layer. With this in mind, we analyzed the effect of adsorption on the viscosity of dilute polymer solutions. The theoretical results obtained could adequately explain the observed abnormalities of viscosity measurements in a quantitative way.

THEORETICAL

General Consideration

In determining the relative viscosity of polymer solutions with a glass capillary viscometer, the flow time of a pure solvent t_0 at a given temperature is a constant. However, if the polymer chains are firmly adsorbed onto the viscometer capillary and the surface of bulb wall during the process of measurement, the effective diameter of the capillary and the volume of the bulb and the wettability of the wall surface to the pure solvent would change. Therefore, the flow time of the solvent is not a true constant but varies with the change in surface properties of the wall. We may regard the flow time of the solvent as a function of polymer concentration denoted by $t_0(C)$.

It is assumed that $t_0(C)$ is directly related to the degree of surface coverage θ of the viscometer by the adsorbed polymer chains and that the flow time of solvent changes linearly from $t_0(0)$ to $t_0(1)$ as θ changes from 0 to 1.

$$t_0(C) = t_0(0) + [t_0(1) - t_0(0)] \cdot \theta \quad (1)$$

If the adsorption process obeys the Langmuir adsorption isotherm,

$$\theta = b \cdot C / [1 + b \cdot C] \quad (2)$$

where b is a parameter related to relative adsorption and desorption rates, the function $t_0(C)$ could be easily deduced. The parameter b may be replaced by its reciprocal C_a :

$$C_a = 1 / b \quad (3)$$

which means that at this particular concentration C_a , $\theta = 1/2$, i.e., half of the available surface is filled with the polymer. Inserting eqs. (2) and (3) into eq. (1) we have:

$$t_0(C) = t_0(0) \cdot [1 + k \cdot C / (C_a + C)] \quad (4)$$

where the constant:

$$k = [t_0(1) - t_0(0)] / t_0(0) \quad (5)$$

denotes the maximum fractional change of flow time of pure solvent due to the variation of the surface properties of viscometer wall in the course of determining polymer solution viscosity. It is worthwhile noting that the constant k may be either positive or negative depending on whether the flow time of the solvent increases or decreases after the adsorption of the polymer.

Ignoring corrections for capillary viscometer such as kinetic energy and drainage correction^[26] and the density difference between solution and solvent, the relative viscosity of the polymer solution is conventionally calculated from the flow time of the solutions $t(C)$ and that of a pure solvent in the clean viscometer $t_0(0)$ as:

$$\eta_r = t(C) / t_0(0) \quad (6)$$

Since the effective flow time of the solvent in the course of measuring solution viscosity is $t_0(0)$ and not $t_0(C)$, the relative viscosity calculated by eq. (6) is only an apparent value, and the true relative viscosity should be:

$$\eta_{r, \text{true}} = t(C) / t_0(C) \quad (7)$$

Combining eqs. (4), (6) and (7), we obtain the relationship between the apparent and true relative viscosity as:

$$\eta_r = \eta_{r, \text{true}} [1 + k \cdot C / (C_a + C)] \quad (8)$$

The above analysis is the starting point of the present discussion. Equation (8) reflects the effect of adsorption on the conventionally measured relative viscosity of polymer solution and may be regarded as the basis for correcting the adsorption effect. Figure 1 demonstrates the general trends of this effect.

Viscosity of Extremely Dilute Solution

Theoretically, in extremely dilute concentration regions both the hydrodynamic and thermodynamic intermolecular interactions are absent, Einstein viscosity law is thus applicable. This is true for solutions of globular solutes with η_r less than 1.1. At this concentration region the relative viscosity varies linearly with concentration and may be expressed as:

$$\eta_{r, \text{theo}} = 1 + [\eta] C \quad (9)$$

from which the intrinsic viscosity:

$$[\eta] = \eta_{sp, \text{theo}} / C = (\eta_{r, \text{theo}} - 1) / C \quad (10)$$

It is reasonable to assign:

$$\eta_{r, \text{true}} = \eta_{r, \text{theo}} \quad (11)$$

Therefore, inserting eq. (9) into eq. (8), we obtain the expression of the conventional reduced viscosity as:

$$\eta_{sp} / C = (\eta_r - 1) / C = [\eta] \{1 + k C / (C_a + C)\} + k / (C_a + C) \quad (12)$$

Equation (12) indicates that the conventional reduced viscosity is no longer a constant equal to $[\eta]$, but varies with polymer concentration. The general pattern of such variations is illustrated in Fig.2, (with given values of $[\eta]$, k and C_a).

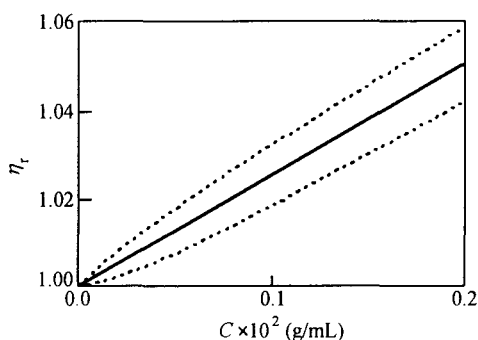


Fig.1 Illustration of the effect of adsorption on the measured relative viscosity of polymer solution with $[\eta] = 25$, $C_a = 5 \times 10^{-5}$.

Middle straight line: hypothetical, $\eta_r = 1 + [\eta]C$; Upper dotted line: maximum 1% increase in flow time of solvent due to adsorption of polymer on viscometer wall surface of viscometer $k = 0.01$; Lower dotted line: maximum 1% decrease in flow time of solvent due to adsorption of polymer on viscometer wall surface of viscometer $k = -0.01$.

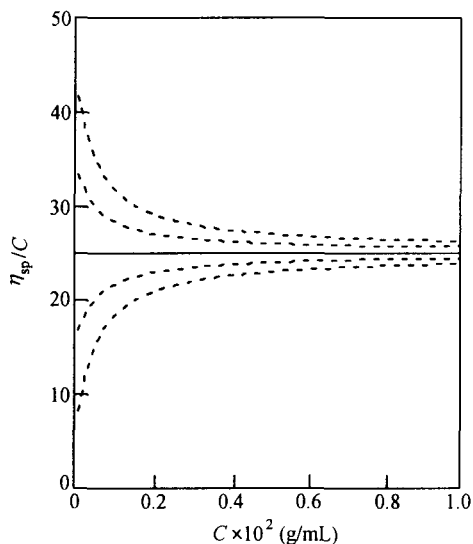


Fig.2 Illustrative plot for variation of reduced viscosity of the polymer solution at extremely dilute concentration regions with $[\eta] = 25$, $C_a = 5 \times 10^{-5}$ and $k = 0.010, 0.005, 0, -0.005$ and -0.010 for curves from top to bottom.

At extremely dilute concentration regions, from eq. (12) we have the extrapolated value of the reduced viscosity to infinitive dilution:

$$I(0) = \lim_{C \rightarrow 0} \eta_{sp} / C = [\eta] + k / C_a \quad (13)$$

The limiting value of reduced viscosity, as concentration approaches infinity or as the reciprocal of concentration approaches zero, is:

$$I(1) = \lim_{C \rightarrow \infty} \eta_{sp} / C = \lim_{1/C \rightarrow 0} \eta_{sp} / C = [\eta] + (1 + k) \quad (14)$$

which is the asymptotic tangent line of the conventional reduced viscosity versus concentration plot. Eq. (12) also shows that as $C = C_a$, the reduced viscosity is the average of $I(0)$ and $I(1)$

$$\eta_{sp} / C_a = [I(0) + I(1)] / 2 \quad (15)$$

Equations (13)~(15) provide a simple graphical procedure to treat the experimental viscosity data in the extreme dilute concentration region: (1) From the η_{sp} / C versus C and η_{sp} / C versus $1/C$ plots, get $I(0)$ and $I(1)$ by the graphical extrapolation method; (2) Using eq. (15) to calculate η_{sp} / C and then using interpolation method on the curve of η_{sp} / C versus C plot, we get C_a ; (3) Subsequently, solving $[\eta]$ and k by eqs. (13) and (14) with known $I(0)$, $I(1)$ and C_a , we have:

$$k = 1/2 \{ [1 - I(0) C_a]^2 - 4 [I(1) - I(0)] C_a \} - 1/2 [1 - I(0)] C_a \quad (16)$$

$$[\eta] = I(1) / (1 + k) \quad (17)$$

There are two alternative methods to estimate C_a from the initial tangent line:

$$(\eta_{sp} / C)_{\text{initial}} = ([\eta] + k / C_a) + (k / C_a^2) (C_a [\eta] - 1) C \quad (18)$$

This meets with the asymptotic tangent line at the crossover concentration C^{**}

$$C^{**} = C_a (19)$$

Though eq. (19) is the exact solution of eqs. (14) and (18), the accuracy of the graphical estimation of C_a depends on the extent to which the experimental data reaches the asymptotic region. Another method is based on the slope of the initial tangent line. Designating it as $S(0)$:

$$S(0) = (k / C_a^2) (C_a [\eta] - 1) \quad (20)$$

and simultaneously solving eqs. (13), (14) and (20), we have:

$$C_a = [I(1) - I(0)] / S(0) \quad (21)$$

but in practice, the arbitrariness of the drawn initial tangent line limits the accuracy of estimating $S(0)$ and hence C_a .

Viscosity in Dilute Solution Region

For the purpose of determining intrinsic viscosities of polymer solutions, measurements are usually carried out at the concentration region with relative viscosities from 1.1 to 2.0. In this dilute solution region, intermolecular interactions are operating and thereby the mathematical representation for relative viscosity should include a higher order term such as:

$$\eta_r, \text{theo} = 1 + [\eta] C + k_H [\eta]^2 C^2 \quad (22)$$

in which k_H is the Huggins slope constant. Inserting eq. (20) into eq. (8), we have the reduced viscosities of dilute polymer solution

$$\eta_{sp} / c = k / (C_a + C) + [\eta] [1 + kC / (C_a + C)] + k_H [\eta]^2 C [1 + kC / (C_a + C)] \quad (23)$$

Equation (23) indicates that the variation of reduced viscosity of the dilute polymer solution with concentration is no longer linear down to an extremely dilute solution. The curves of reduced viscosity plotted against concentration will show either an upward or a downward turn depending on whether the constant k is positive or negative as the concentration is below a certain critical value. These features are illustrated in Fig.3.

From eq. (23), it is easy to deduce the initial tangent line of reduced viscosity versus concentration plots as C approaches zero at extremely dilute regions and the asymptotic tangent line of the reduced viscosity curve as C approaches infinity as:

Initial tangent line:

$$(\eta_{sp}/C)_{INIT} = ([\eta] + k/C_a) + (k_H [\eta]^2 + [\eta]k/C_a - k/C_a^2) C \quad (24)$$

Asymptotic tangent line:

$$(\eta_{sp}/C)_{ASYMP} = (1+k) [\eta] - k_H [\eta]^2 C_a + (1+k) k/C_a - k_H [\eta]^2 C \quad (25)$$

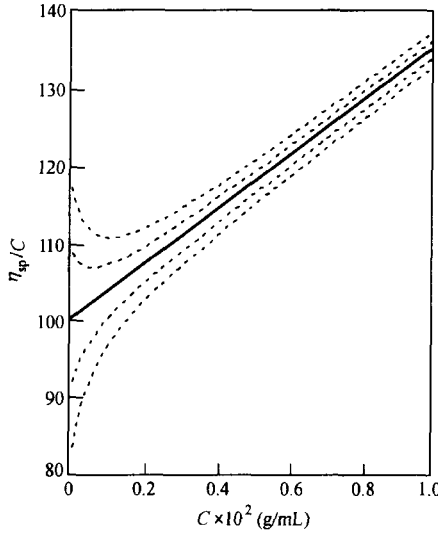


Fig.3 Illustration of the effect of adsorption on the reduced viscosity of dilute polymer solution with $C_a = 5 \times 10^{-4}$ g/mL, $[\eta] = 100$, $k_H = 0.35$ and from upper down to bottom line $k = 0.010, 0.005, 0, -0.005, -0.010$.

The crossover concentration C^{**} of these two straight lines could be simply obtained from eqs. (24) and (25) as $C^{**} = C_a$, which is identical with eq. (19) for the solution at extremely dilute concentration region. From the slope of the initial tangent line $I(0)$, $S(0)$ and of the asymptotic tangent line $I(1)$, $S(1)$:

$$\begin{aligned} I(0) &= [\eta] + k/C_a \\ S(0) &= k_H [\eta]^2 + [\eta] k/C_a - k/C_a^2 \\ I(1) &= (1+k) [\eta] - k k_H [\eta]^2 C_a \\ S(1) &= (1+k) k_H [\eta]^2 \end{aligned}$$

we have:

$$C_a = [I(1) - I(0)] / [S(0) - S(1)] \quad (26)$$

and parameter k may be obtained by solving equation

$$(1+k)^3 - [I(0) C_a + 1] (1+k)^2 + [C_a^2 S(1) + C_a I(1)] (1+k) - C_a^2 S(1) = 0 \quad (27)$$

with evaluated C_a value. Then the intrinsic viscosity and Huggins slope constant may be calculated by

$$[\eta] = I(0) - k/C_a \quad (28)$$

$$k_H = S(1) / (1+k) \quad (29)$$

It is noteworthy that the intercept and slope of the asymptotic tangent line in the region with $C \gg C_a$ are both increased or decreased by a factor of $(1+k)$. This factor should be considered as the correction factor for the effect of adsorption of polymers on the wall surface of the viscometer at the concentration region conventionally used for intrinsic viscosity determination. We believe that the adsorption effect is unavoidable in most cases. However, it has unfortunately been overlooked for many years.

EXPERIMENTAL

Materials

Six commercial reagent grade polyethylene glycol samples were used. These samples were characterized by VPO and SEC. The results obtained are listed in Table 1. The aqueous stock solutions of PEG were prepared by weighing thoroughly dried samples and then boiling them in a solution. The weight concentration $C_w(\text{g/g})$ of PEG were converted to weight-volume concentration $C(\text{g/cm}^3)$ through its density-concentration relation

$$\rho = \rho_0(1 + a C_w) \quad (30)$$

In which ρ_0 is the density of pure water and constant $a = 0.1866$ as determined by the pycnometer method.

Table 1. The molecular weights of PEG samples

PEG	Nominal mol. wt.	M_n , VPO	M_w / M_n , SEC
A	400	---	---
B	1000	1060	1.58
C	4000	3795	1.43
D	6000	4733	1.82
E	10000	9150	1.34
F	20000	21090	1.75

The poly(vinyl alcohol) (PVA) sample used in this work was a commercial product. The degree of polymerization (DP) of PVA ranges from 2400 to 2500 and the degree of saponification (D.S) from 98.0 to 99.0 mol%. A known amount of PVA was dissolved in distilled water under reflux for 2 h to prepare the stock solution, and its concentration was determined by weighing.

Viscosity

Two Ubbelohde dilution type viscometers were used, one for PEG, the other for PVA. The flow times of freshly distilled water in the thoroughly cleaned viscometer for PEG were measured in the temperature range of 10°C to 60°C and compared with the flow times measured for water in a standard viscometer to determine the instrumental constants for the coupled kinetic energy and drainage corrections of the working viscometer^[26]. The flow time of water in a thoroughly cleaned viscometer at 25°C was 86.6 s. The flow time of water increased to 87.6 s if the viscometer was only cleaned by repeated soaking and rinsing with water at ambient temperatures. That the wettability of the inner wall surface of the viscometer to water had also changed was apparent from visual inspection of the adhered water layer. If the viscometer was cleaned using boiling water, the flow time and wettability reverted to its original state. Therefore the flow time of a known amount of water in the viscometer was first measured in order to check the cleanliness and then weighed amounts of stock solutions were added into the viscometer successively so as to determine the solution viscosity.

The relative viscosities of PEG solutions were calculated according to

$$\eta_r(C) = \frac{\rho}{\rho_0} \frac{t(C)}{t_0(0)} \frac{A - B/t^2(C) - C/t^4(C)}{A - B/t_0^2(C) - C/t_0^4(C)} \quad (31)$$

in which A , B and C are predetermined instrumental constants of the working viscometer.

The viscosity determination for aqueous solutions of PVA was carried out at 30°C. The viscometer used in this case has much longer flow time, so K.E. and drainage corrections can be ignored. The flow time of water in the thoroughly cleaned viscometer is 310.78 ($s = 0.03$) s. This increased to 311.43 ($s = 0.08$) s for a viscometer washed with cold water after contact with PVA solution. The flow time of water reconverted to original value when the viscometer was washed

with boiling water. The procedure for determining solution viscosity is similar to that for the PEG solution, but the relative viscosities were calculated simply as the ratio of the flow time of solution to that of solvent.

RESULTS AND DISCUSSION

The dependence of the relative viscosities of aqueous PEG solutions on concentration is shown in Fig.4. We can immediately see the nearly perfect linearity of the variation of relative viscosity with concentration. However, the results of linear regression analysis listed in Table 2 showed that though all the linear correlation coefficients were greater than 0.999, the straight lines never pass through the origin ($\eta_r = 1$ at $C = 0$) but intersected with the η_r axis at points slightly greater than one. The plots of reduced viscosity against concentration were shown in Fig.5. The curves showed upward turns at extremely dilute concentration region for all the samples, similar to those curves with positive k as discussed in the theoretical section. Treating the experimental data by the graphic procedures outlined above, the extrapolated and interpolated values of $I(0)$, $I(1)$ and C_a are listed in Table 2, from which k and $[\eta]$ is evaluated by eqs. (16) and (17). The results obtained are also listed in the same table. The accuracy of graphic extrapolation and / or interpolation may be limited, but the evaluated values of C_a , k and $[\eta]$ could adequately describe all the viscosity data, as shown by the calculated lines of relative viscosities and reduced viscosities according to eqs. (8) and (12) in Figs.4 and 5.

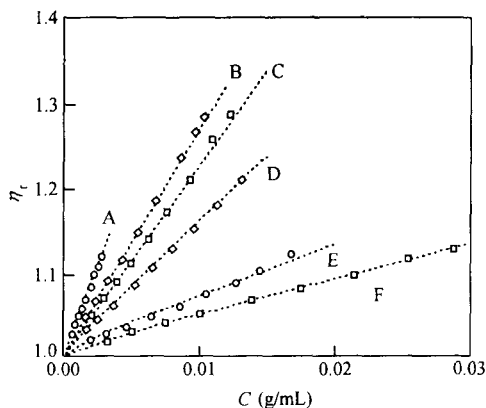


Fig.4 Concentration dependence of relative viscosities of polyethylene glycol aqueous solution.

Experimental points: calculated with the flow time of the solution and pure water in thoroughly cleaned viscometer, corrected for kinetic energy and drainage; Lines: calculated by eq. (8) with evaluated $[\eta]$, k and C_a .

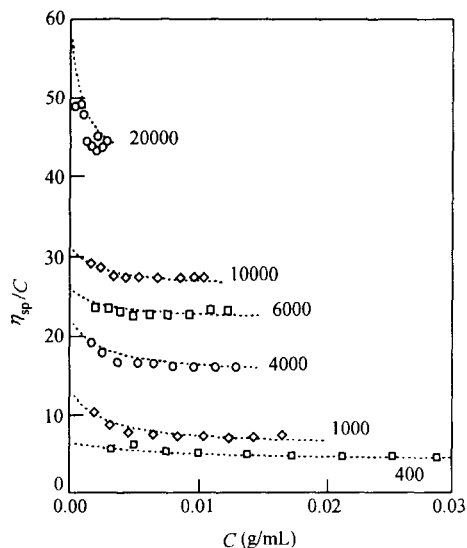


Fig.5 The reduced viscosity versus concentration plot for aqueous polyethylene glycol solution.

Dotted line: calculated by eq. (12) with evaluated k , C_a and $[\eta]$.

The viscosity of dilute aqueous polyvinyl alcohol solution in the concentration range with relative viscosity from 1.1 to 1.6 was first measured to estimate the intrinsic viscosity and overlap concentration^[27]. Linear extrapolation in this concentration range gave $[\eta] = 97$ mL/g. Measurements were extended to the extremely dilute concentration range with relative viscosity less than 1.1. The reduced viscosity so obtained was collated with previously obtained values and

plotted against concentration as shown in Fig.6. It can be seen that a rather sharp upward curve appears at extremely dilute concentration region, similar to those observed by previous investigators in the same concentration region. By the data treatment procedures outlined in the theoretical section, for the whole concentration range of aqueous polyvinyl alcohol solution studied we found $k = 0.001$, $C_a = 4.1 \cdot 10^{-5}$, $[\eta] = 95.6$ and $k_H = 0.51$. Using these parameters, the reduced viscosity curve calculated according to eq. (23) is also shown in Fig.6. This fitted well with the experimental points.

The fitness of calculated curve to experimental data is only phenomenal. The most encouraging fact is that the evaluated parameter k is in agreement with the direct measured value from the changes of flow time of the solvent after measuring solution viscosity. For example, the fractional increasing of flow time of water in viscometer for aqueous PEG solution is 0.012 while the average value of k in Table 2 is 0.014. The fractional increasing of flow time of water in viscometer for aqueous PVA solution is 0.002 while $k = 0.01$. Therefore, we can conclude that the mathematical analysis in the present article is correct and the abnormality of reduced viscosity appearing in regions of extremely dilute concentration region is solely due to the effect of adsorption of polymer chains on the inner surface of viscometer.

Table 2. The derived viscosity data of aqueous PEG solutions

PEG	Linear regression for η_r -C lines					Graphic evaluation		
	Intercept	Slope	Corr. coef	$l(0)$	$l(1)$	C_a (g/mL)	k	$[\eta]$ (mL/g)
A	1.0075	4.26	0.9992	6.5	4	0.0008	0.0206	3.90
B	1.0050	6.81	0.9987	13	6	0.0025	0.0178	5.90
C	1.0058	15.51	0.9999	22	15	0.0025	0.0182	14.73
D	1.0011	22.85	0.9996	26	22	0.0025	0.0106	21.77
E	1.0024	27.07	1.0000	31	26	0.0025	0.0134	25.66
F	1.0038	42.51	0.9989	58	40	0.001	0.0187	26

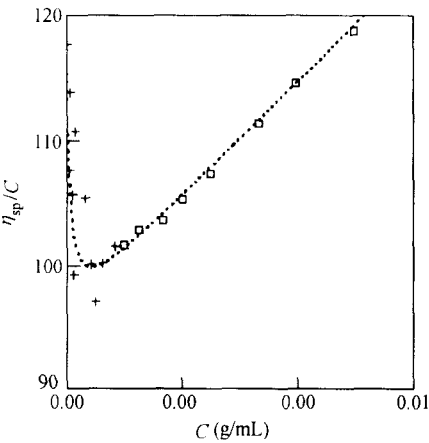


Fig. 6 The reduced viscosity versus concentration plot for aqueous polyvinyl alcohol solutions. Box points: in dilute concentration region, $\eta_r > 1.1$ ^[27]; Cross points: at extremely dilute concentration regions, $\eta_r < 1.1$; Dotted line: calculated according to eq. (23), with evaluated viscometric parameters $[\eta]$, k_H , k and C_a

Another interesting problem concerns the specific concentration C_a . These values are in the same order of magnitude as that of the critical concentrations for coil shrinking C_s ^[28, 29]. The values of C_a for aqueous PEG solution in Table 2 decreases with increasing molecular weight. This is also

in agreement with C_s of PEG tetrahydrofurane as determined by size exclusion chromatography. The resemblance between C_a and C_s will encourage more researchers to conduct further investigations into their properties and their natures.

The effects of adsorption are usually ignored in traditional viscometry for polymer solution. As analyzed in the theoretical section and illustrated by experimental results, in concentration regions conventionally used intrinsic viscosity, an error as high as 1 to 2 percent in both intrinsic viscosity and slope constant may arise. Since adsorption is unavoidable, we may conclude that it is necessary to correct the viscosity of dilute polymer solution measured by glass capillary viscometer for adsorption in all cases.

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