

Introduction of a Reliable Method for Determination of Intrinsic Viscosity for Any Polymer with High Precision^{*}

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Abstract Intrinsic viscosities for a given polyelectrolyte in salt free and low-salt solvents reported in literatures are normally not comparable, because of inadequate valuation procedures. This article describes a theoretically justified reliable method, which is free of any model assumptions: The so called Wolf plot (logarithm of the relative viscosity as a function of polymer concentration) enables the unequivocal determination of intrinsic viscosities for all kinds of macromolecules, irrespective of whether they are chain molecules of different architecture or globular polymers, whether they are charged or uncharged. The validation of the method was examined by evaluation of the viscosities of a polyelectrolyte, some uncharged polymers of different architectures, uncharged polymer blends, and some literature data.

Keywords: Intrinsic viscosity; Polyelectrolyte; New method; Wolf plot; Introduction.

INTRODUCTION

The importance of intrinsic viscosity can hardly be overestimated in the academic field as well as for technical applications. The intrinsic viscosity of a certain polymer in a given solvent at temperature T is defined as:

$$[\eta] \equiv \lim_{c \rightarrow 0} \frac{\ln \eta_{\text{rel}}}{c} \equiv \lim_{c \rightarrow 0} \frac{\eta_{\text{sp}}}{c} \quad (1)$$

where η_{rel} is the relative viscosity of a polymer solution when compared with the pure solvent, and η_{sp} ($\eta_{\text{sp}} = \eta_{\text{rel}} - 1$) is the relative increase in viscosity of the polymer solution with a concentration c (mass per volume).

According to Eq. (1), the intrinsic viscosity $[\eta]$ of a polymer can be obtained by extrapolating the $\frac{\ln \eta_{\text{rel}}}{c}$ or the

$\frac{\eta_{\text{sp}}}{c}$ to infinite dilution ($c \rightarrow 0$). Based on numerous experimental results, several empirical equations have been established to obtain $[\eta]$ such as the famous Huggins equation, Eq. (2), and Kraemer equation, Eq. (3)

$$\frac{\eta_{\text{sp}}}{c} = [\eta] + k_{\text{H}} [\eta]^2 c \quad (2)$$

^{*} This work was financially supported by the National Natural Science Foundation of China (No. 51273166), the National Basic Research Program of China (No. 2010CB732203) and the Scientific and Technological Innovation Platform of Fujian Province of China (No. 2009J1009).

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Received May 2, 2013; Revised May 29, 2013; Accepted June 9, 2013

doi: 10.1007/s10118-014-1388-y

$$\frac{\ln \eta_{\text{rel}}}{c} = [\eta] - \beta [\eta]^2 c \quad (3)$$

where k_H and β are Huggins constant and Kraemer constant, respectively. By comparing the running time of polymer solution (t) with that of pure solvent (t_0) through capillary of a capillary viscometer, η_{rel} of a polymer solution can be easily obtained:

$$\eta_{\text{rel}} = \frac{\eta}{\eta_s} = \frac{t}{t_0} \quad (4)$$

This relation holds true in most cases when t_0 is over 100 s.

The above relations have been successfully applied to obtain $[\eta]$ for uncharged polymers, while the dependences of $\frac{\ln \eta_{\text{rel}}}{c}$ or $\frac{\eta_{\text{sp}}}{c}$ on c remain linear over the experimentally studied composition range, even at high dilution. However, those linear extrapolations of the above mentioned zero-divided-by-zero types often fail when a polyelectrolyte is concerned^[1, 2], because the electrostatic repulsion between the charged groups of polyelectrolyte increases strongly upon dilution. Extra salt has been suggested to be added into polyelectrolyte solution, so that the electrostatic repulsion would be shielded due to the increased ionic strength and the viscosity behavior of charged polymer would be “normal”. However, this brings in some questions such as: is thus obtained intrinsic viscosity the true $[\eta]$ of the polyelectrolyte, which kind of and how much extra salt should be added. Fuoss and Strauss^[3] suggested another equation in order to obtain $[\eta]$ of polyelectrolytes and it reads:

$$\left(\frac{\eta_{\text{sp}}}{c} \right)^{-1} = [\eta]^{-1} (1 + k_{\text{FS}} \sqrt{c}) \quad (5)$$

where k_{FS} is a constant in analogy to k_H . This method is presently used quite often even though non-linear extrapolation of $(\frac{\eta_{\text{sp}}}{c})^{-1}$ versus c at every high dilution ($c < 10^{-5}$ g/mL)^[2, 4, 5] has been observed.

Recently, Wolf has applied the tools of phenomenological thermodynamics to the viscosity of polymer solutions, and considered that the viscosity of polymer solutions constitutes a function of state to obtain the following expression for $d \ln \eta$ ^[2]

$$d \ln \eta = \left(\frac{\partial \ln \eta}{\partial c} \right)_{T, p, \dot{\gamma}} dc + \left(\frac{\partial \ln \eta}{\partial T} \right)_{c, p, \dot{\gamma}} dT + \left(\frac{\partial \ln \eta}{\partial p} \right)_{c, T, \dot{\gamma}} dp + \left(\frac{\partial \ln \eta}{\partial \dot{\gamma}} \right)_{c, T, p} d\dot{\gamma} \quad (6)$$

The first partial differential represents the specific hydrodynamic volume of the polymer at polymer concentration c at temperature (T), pressure (p), and shear rate ($\dot{\gamma}$), and can be understood as a generalization of the intrinsic viscosity of the polymer for arbitrary concentration (quantifying the specific hydrodynamic volume under these conditions), which is denoted as $\{\eta\}$.

$$\left(\frac{\partial \ln \eta}{\partial c} \right)_{T, p, \dot{\gamma}} = \{\eta\} \quad (7)$$

According to the definition of intrinsic viscosity, *i.e.* Eq. (1), $\{\eta\}$ becomes $[\eta]$ in the limit of infinite dilution and vanishing shear rate

$$\lim_{\substack{c \rightarrow 0 \\ \dot{\gamma} \rightarrow 0}} \{\eta\} = [\eta] \quad (8)$$

The above equation suggests directly determining $[\eta]$ from viscosities of polymer solution. Namely, by plotting $\ln \eta$ or $\ln \eta_{\text{rel}}$ as a function of c ($\frac{\partial \ln \eta}{\partial c} = \frac{\partial \ln \eta_{\text{rel}}}{\partial c}$), the initial slope of the dependence can be obtained to give the

intrinsic viscosity $[\eta]$ directly. The advantages of this novel approach is free of any model assumption, and more importantly it avoids the magnification of experimental errors resulted from the zero-divided-by-zero types of the traditional methods.

By employing the Huggins equation, Eq. (2), we obtain

$$\{\eta\} = \frac{[\eta](1 + 2k_H[\eta]c)}{1 + [\eta]c(1 + k_H[\eta]c)} \quad (9)$$

and a first order expansion of the equation yields

$$\{\eta\} = [\eta] + (2k_H - 1)[\eta]^2 c + \dots \quad (10)$$

By employing the Kraemer equation, Eq. (3), we obtain

$$\{\eta\} = [\eta] - 2\beta[\eta]^2 c \quad (11)$$

With the two parameters of $[\eta]$ and k_H or β , Eqs. (10) and (11) suffice to describe the composition dependence of the specific hydrodynamic volume $\{\eta\}$ within the region of pair interaction of uncharged polymer in solution. However, those two parameters are not enough for charged polymer because of the electrostatic repulsion induced expansion of the charged groups. It has been assumed that $\{\eta\}$ of charged polymer decreased from $[\eta]$ at infinite dilution to a constant value of $[\eta]^\pm$ at sufficiently high ionic strength by increase of polymer concentration or additional salt. At the same time, the decrease from $[\eta]$ to $[\eta]^\pm$ is assumed to obey an exponential transition in the composition range A

$$\{\eta\} = ([\eta] - [\eta]^\pm) e^{-\frac{([\eta] - [\eta]^\pm)c}{A}} + [\eta]^\pm \quad (12)$$

It can be rewritten as

$$\{\eta\} = [\eta] \left(p e^{-\frac{pc[\eta]}{A}} + (1 - p) \right) \quad (13)$$

where $p = \left(\frac{[\eta] - [\eta]^\pm}{[\eta]} \right)$. The composition dependence of η_{rel} can therefore be obtained by integration of Eq. (11), which reads

$$\ln \eta_{\text{rel}} = A \left(1 - e^{-\frac{pc[\eta]}{A}} \right) + (1 - p)c[\eta] \quad (14)$$

Integration of Eq. (9) by adding a quadratic term in c to denominator and a characteristic specific hydrodynamic volume $[\eta]^*$ in analogy to $[\eta]^\pm$, one obtains

$$\ln \eta_{\text{rel}} = \frac{c[\eta] + Bc^2[\eta][\eta]^*}{1 + Bc[\eta]} \quad (15)$$

where B is a system specific constant. The comparison of the Taylor expansion of Eq. (15) and Eq. (2) leads to

$$B = \frac{0.5 - k_H}{1 - ([\eta]^* / [\eta])} \quad (16)$$

Both Eqs. (14) and (15) require three parameters to obtain intrinsic viscosity for polyelectrolyte, which can be easily determined on a PC from a sufficiently large number of viscosity measurements at different polymer concentrations by any fitting program. Those equations have been successfully utilized to describe the dependence of η_{rel} on c for quite a few types of polyelectrolytes precisely^[2, 6-13].

For uncharged polymer, $[\eta]^*$ is found to be 0^[14, 15], so Eq. (15) turns into

$$\ln \eta_{\text{rel}} = \frac{c[\eta]}{1 + Bc[\eta]} \quad (17)$$

In this paper, the viscosities of a polyelectrolyte, some uncharged polymers of different architectures and polymer blends in different solvents were measured, and the obtained data were evaluated using the Wolf plot equations (Eqs. (14), (15) and (17)). Moreover, some literature data were evaluated by the Wolf equations too. The obtained intrinsic viscosities were compared with those obtained by the traditional ways in order to suggest the reliability of the new method.

EXPERIMENTAL

Materials

Poly(styrene sulfonate) sodium salt (PSS-Na, Lot#pss200305) with a weight-average molecular weight (M_w) of 75.6 kg/mol and polydispersity index (M_w/M_n , M_n is number-average molecular weight) of lower than 1.20 was purchased from Polymer Standard Service (PSS, Mainz, Germany). Linear polybutadiene (PB, lot# STNO 4512F, $M_w = 132.2$ kg/mol, $M_w/M_n = 1.08$) and three-armed star polybutadiene (PB*, lot STNO 4512K, $M_w = 65.3$ kg/mol, $M_w/M_n = 1.22$) were kindly donated by Lanxess Deutschland GmbH. Polystyrene (PS, $M_w = 240$ kg/mol, $M_w/M_n = 1.80$) and poly(vinyl methyl ether) (PVME, $M_w = 87$ kg/mol, $M_w/M_n = 1.36$) were obtained from the former Hüls AG and BASF, respectively. Linear poly(styrene-block-butadiene) copolymer [(SB)2, $M_w = 85.5$ kg/mol, $M_w/M_n = 1.12$] was anionically polymerized with a butadiene content of 74.2 mol%. Tetrahydrofuran (THF), cyclohexane (CH), toluene (TL) and sodium chloride (NaCl) were of p.a. quality and were purchased from Sigma-Aldrich. The used deionized water was treated with Millipore-Q water purification system.

Methods

PSS-Na was dissolved in pure water or NaCl aqueous solutions, and their viscosities were measured at 25 ± 0.1 °C using Ubbelohde capillary viscometer (0a, capillary diameter of 0.53 mm) in combination with an automatic viscosity measurement system (Schott Instruments, Mainz, Germany). The viscosities of other polymers dissolved in organic solvents were measured using another Ubbelohde capillary viscometer (0c, capillary diameter of 0.46 mm), respectively.

The obtained data were evaluated by the traditional methods and by the Wolf plot equations. Some literature data were extracted using a software of GetData Graph Digitizer (Version 2.22, S. Fedorov, Russia), and were evaluated by the Wolf plot equations too.

RESULTS AND DISCUSSION

Figure 1 shows the concentration dependences of η_{sp}/c for PSS-Na in NaCl aqueous solvents, which is the traditional way (Huggins plot) to obtain intrinsic viscosity. It is very obvious that the ionic strength in the polyelectrolyte solution influences the viscosity behavior of the solute greatly. It is hard to extrapolate the composition dependences of η_{sp}/c to infinite dilution, especially if the dependence is markedly curved under low ionic strength and/or in the highly dilute region. This situation leads to difficulties to determine the intrinsic viscosities of the polyelectrolytes in the traditional way.

The obtained data were also plotted according to the Fuoss and Strauss method, as shown in Fig. 2. It can be seen that linear regression for different constant ionic strengths is fairly reached. Thus obtained intrinsic viscosities, their standard errors and the linear regression correlation coefficients (R^2) are collected in Table 1. It is worth pointing out that the extrapolation of the dependences of $(\eta_{\text{sp}}/c)^{-1}$ on $c^{1/2}$ to $c \rightarrow 0$ leads to extremely small intercept values for the pure water and 10^{-4} mol/L NaCl solvent cases. The intrinsic viscosities are the reciprocals of the intercepts, meaning that very small experimental uncertainties would lead to large errors of the intercept, *i.e.* in the resultant $[\eta]$. This is evidenced by the obtained $[\eta]$ of 34550 mL/g with a huge error of 41060 mL/g (*ca.* 120%) for the pure water solvent system, and $[\eta]$ of 2000 mL/g with an error of 54 mL/g

(2.7%) for the 10^{-4} mol/L NaCl solvent system, even though the regression correlation coefficients are close to 1. Those results clearly demonstrate the problem caused by the zero-divided-by-zero types of the method. Meanwhile, it is also worth mentioning that running time decreased gradually with the repeating measurements for a same solution. For example, the running time of the first measurement for the highest concentration of PSS-Na in pure water (389.57 s) was 2.22 s longer than its fifth measurement. This phenomenon is understood to be caused by the increase of ionic strength resulted from the dissolution of CO_2 in the solution, which indicates inevitable uncertainty of measurement during experimental procedure.

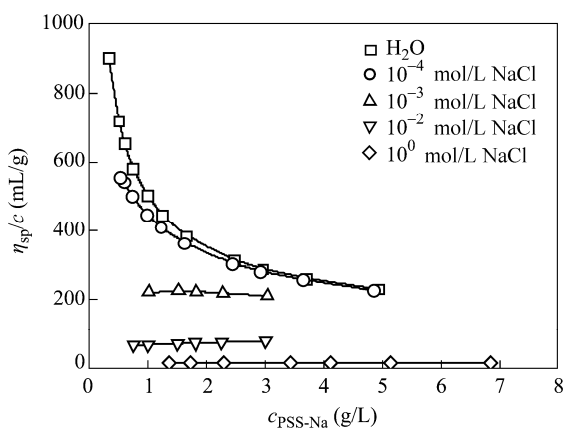


Fig. 1 Concentration dependences of η_{sp}/c (Huggins plot) for PSS-Na in aqueous NaCl solvents (The curves are to guide the eyes.)

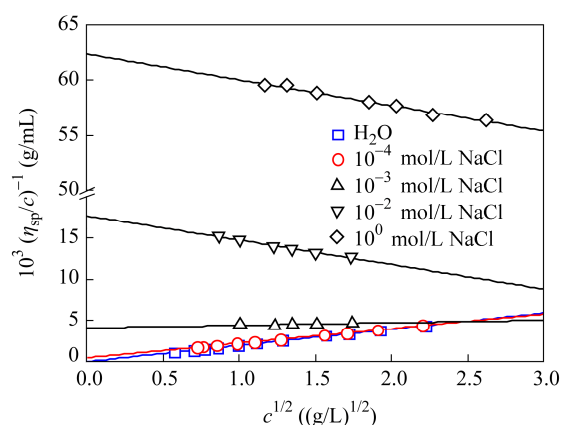


Fig. 2 Dependences of $(\eta_{sp}/c)^{-1}$ on $c^{1/2}$ for PSS-Na in aqueous NaCl solvents. The lines are linear regressions of the data points using the Fuoss and Strauss equation [Eq. (5)].

Figure 3 shows the Wolf plot of the PSS-Na in aqueous NaCl solvents, *i.e.* $\ln \eta_{rel}$ versus c dependencies. The curves are calculated by fitting the parameters of Eq. (15) to the data points. The most obvious result of the graph consists in the wonderful fitting of each set of data points by the Wolf plot equation. The fitting parameters together with their standard errors and the correlation coefficients (R^2) are summarized in Table 1. It is seen that the errors for each parameter are relatively small. Compared with the results evaluated using the Fuoss and Strauss method, the $[\eta]$ values evaluated by the Wolf plot method are much lower. The most striking point is the low errors of 5.8% for the pure water solvent system and of 1.8% for the 10^{-4} mol/L NaCl solvent system, which are much lower than those evaluated by the Fuoss and Strauss method. Plus, the correlation coefficients for all the solvent systems are very close to 1, and in most cases are higher than those of Fuoss and Strauss method. Moreover, the $[\eta]$ values are comparable under higher ionic strengths for both methods, while the Wolf plot results are with lower errors. Those results suggest the high reliability of the Wolf plot method.

Table 1. Parameters for PSS-Na in different solvents^a

Solvent	Wolf plot				Fuoss-Strauss plot	
	$[\eta]$	$[\eta]^*$	B	R^2	$[\eta]$	R^2
H ₂ O	1448 ± 84	70.8 ± 3.3	2.12 ± 0.08	0.9885	34550 ± 41060	0.9985
10^{-4} mol/L NaCl	786 ± 14	56.6 ± 2.0	1.70 ± 0.04	0.9999	2000 ± 54	0.9998
10^{-3} mol/L NaCl	235 ± 6	0	0.606 ± 0.046	0.9988	243 ± 14	0.5359
10^{-2} mol/L NaCl	69.8 ± 0.7	0	0	0.9997	56.8 ± 0.6	0.9918
10^0 mol/L NaCl	16.9 ± 0.02	0	0	0.9961	16.0 ± 0.06	0.9842

^a The unit of $[\eta]$ and $[\eta]^*$ is mL/g.

Figure 4 shows the evaluations of data taken from the literatures^[16–20] by the Wolf plot method, and Table 2 lists the corresponding parameters. It is surprising to find that all sets of data points can be well fitted by the Eq. (15), irrespective of the type of polyelectrolyte (polyanion or polycation, and natural or synthetic polymer) and the type of solvent (water, organic solvent or mixture solvent). It is also seen that the errors of the parameters are relatively small, and the correlation coefficients are very close to 1, indicating high reliability of the method. Table 2 also lists the intrinsic viscosities reported in the literatures, which were obtained by using the Fuoss and Strauss method^[17, 18] or modified Fuoss and Strauss method^[16, 20]. Some more literature results concerning viscosities of polyelectrolytes^[21, 22] and polysaccharides^[23–25] have also been well fitted by the Wolf plot method with high accuracy, and no exception has been found so far.

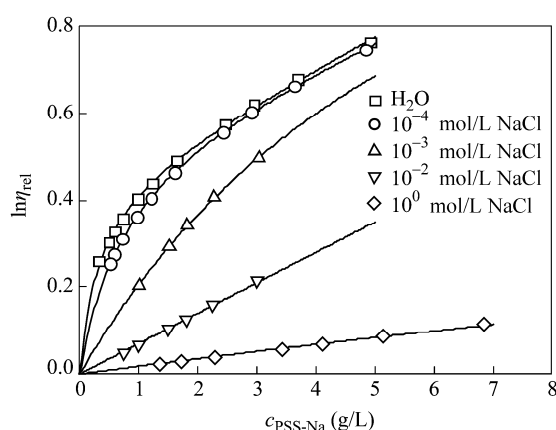


Fig. 3 Concentration dependences of the $\ln \eta_{\text{rel}}$ for PSS-Na in aqueous NaCl solvents. The curves are calculated by fitting the parameters of Eq. (15) to the data points.

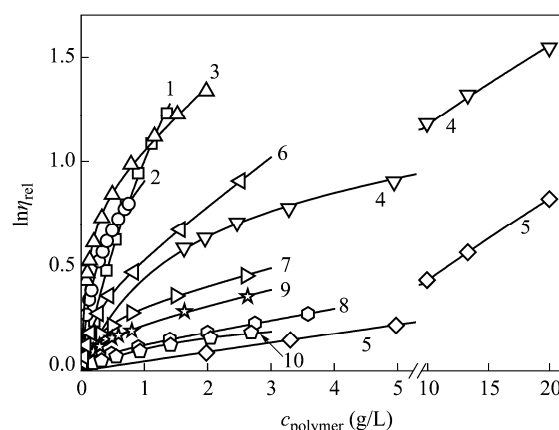


Fig. 4 Evaluations of the data extracted from the literatures^[16–20] by the Wolf plot method. The curves are calculated by fitting the parameters of Eq. (15) to the data points, respectively. The polyelectrolyte/solvent system number of the data-points and the corresponding parameters are collected in Table 2.

Table 2. The data and curve No., polyelectrolyte/solvent systems, the parameters extracted from the viscosity results of the literatures^[16–20] and the corresponding reference values (The unit of $[\eta]$ and $[\eta]^*$ is mL/g.)

No.	System ^a	Wolf plot parameters				Ref $[\eta]$	Ref
		$[\eta]$	$[\eta]^*$	B	R^2		
1	Chitosan/1% acetic acid	1339 ± 62	0	0.251 ± 0.034	0.9968	2200	16
2	Alginate/H ₂ O	4441 ± 124	317 ± 29	1.354 ± 0.056	0.9997	700	16
3	Qcell/H ₂ O	9164 ± 566	277 ± 18	1.147 ± 0.041	0.9982	11172	17
4	PDDA/H ₂ O	744 ± 40	32.8 ± 1.6	0.995 ± 0.033	0.9991	3136 ^b	18
5	PDDA/1 mol/L NaCl	45.6 ± 0.4	0	0.120 ± 0.012	0.9999	40.6 ^b	18
6	CMC-Na/10% acetonitrile-water	2073 ± 102	227 ± 7	2.484 ± 0.117	0.9997	—	19
7	P2VMP/H ₂ O	1245 ± 79	78.3 ± 5.8	3.412 ± 0.194	0.9991	118.6	20
8	P2VMP/methanol	392 ± 35	54.0 ± 1.0	10.00 ± 0.69	0.9963	62.9	20
9	P2VBP/H ₂ O	749 ± 43	71.0 ± 4.0	4.768 ± 0.313	0.9988	96.4	20
10	P2VBP/methanol	154 ± 14	0	3.163 ± 0.327	0.9883	74.8	20

^a Qcell: quaternized cellulose; PDDA: poly(dimethyldiallyl ammonium chloride); CMC-Na: sodium carboxymethyl cellulose; P2VMP: poly-2-vinyl-*N*-methyl pyridinium bromide; P2VBP: poly-2-vinyl-*N*-*n*-butyl pyridinium bromide.

^b The literature^[18] does not provide those results, and they are obtained directly from the literature graph using the Fuoss and Strauss method evaluation (Eq. (5)).

Viscosities of some uncharged polymers such as homopolymers in different solvents were measured, and the data were evaluated by the Wolf plot method (Eq. (17)) and were also evaluated by the traditional ways such as the Huggins plot and the Kraemer plot methods. Thus obtained results are summarized in Table 3. Figure 5 shows the Wolf plot of some of the polymer/solvent systems and the corresponding calculated curves. Those systems are chosen with the intention to represent typical polymer/solvent systems such as homopolymer/good solvent (PS, linear and three armed PB/THF), homopolymer/ θ solvent (PS/CH), block copolymer/good solvent [(SB)2/THF] or selective solvent [(SB)2/CH], and polymer blend/solvent (PS/PVME/THF), which are highly and widely interesting presently. The obvious is the well-fitting of each set of the data points by the Wolf plot equation. It is seen that the thus obtained $[\eta]$ values are within the standard errors identical with the corresponding results evaluated by the traditional methods, irrespective of polymer molecular architecture, polymer kind, solvent type or polymer blend, indicating the high accuracy of the Wolf plot method. At the same time, the correlation coefficient of the Wolf plot method for each polymer/solvent system is very close to unity, and is in all cases higher than those of the traditional methods. It is noted that the correlation coefficients for the PB/THF, (SB)2/CH, PS/PVME/CH and PVME/CH systems evaluated by the traditional methods are very low, suggesting low reliability of the linear regressions of those data, respectively. However, when the same data were evaluated by the Wolf plot method, the correlation coefficients are much higher to be very close to 1, directly displaying the advantage of avoiding the zero-divided-by-zero type extrapolation. Moreover, the Huggins constants were obtained by the Wolf plot method using Eq. (16), and are within the standard errors comparable with the k_H obtained directly from the Huggins equation in most cases. It is noted that the k_H values evaluated by Huggins method are respective of 1.336 and 0.516 for the (SB)2/CH/25 °C and PS/CH/55 °C systems, and are very unusual. It has been pointed out that k_H is 0.5–0.7 for θ solvent, and < 0.5 for good solvent^[1, 26]. Therefore, the k_H value of 0.623 for the (SB)2/CH/25 °C system and 0.426 for the PS/CH/55 °C system evaluated by the Wolf plot method are more reasonable, because CH is a good solvent for the polybutadiene block in the former system and the temperature is higher than θ (34.5 °C) for the latter. The above analysis suggests that the Wolf plot method is also suitable to obtain intrinsic viscosity and Huggins constant for uncharged polymer. For the solutions of uncharged polymers the B values are close to zero, implying that the viscosity for a given concentration of a polymer solution can be estimated very accurately once its intrinsic viscosity is known.

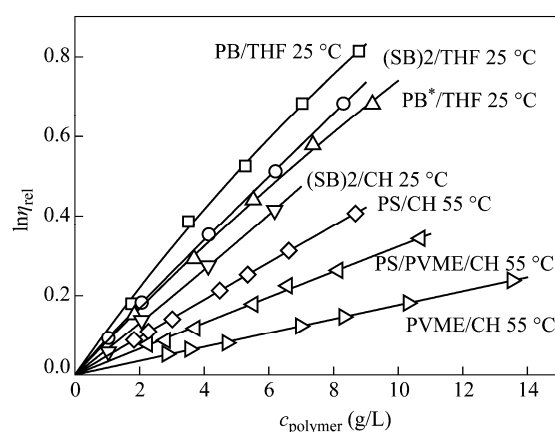


Fig. 5 Concentration dependences of $\ln \eta_{rel}$ for some uncharged polymers
The curves are calculated by fitting the parameters of Eq. (17) to the data points.

Table 3. Parameters for uncharged polymer systems

System	Wolf plot				Huggins plot			Kraemer plot	
	$[\eta]$	B	k_H	R^2	$[\eta]$	k_H	R^2	$[\eta]$	R^2
PB/THF/25 °C	115.6 ± 5.2	0.244 ± 0.054	0.256	0.9980	111.0 ± 6.8	0.315	0.7851	109.3 ± 4.8	0.6038
(SB)2/THF/25 °C	88.2 ± 1.6	0.107 ± 0.030	0.393	0.9998	89.6 ± 1.4	0.398	0.9794	90.0 ± 0.8	0.9410
PB*/THF/25 °C	86.4 ± 3.3	0.195 ± 0.059	0.305	0.9985	84.0 ± 2.5	0.373	0.9309	83.9 ± 1.5	0.8339
(SB)2/CH/25 °C	63.9 ± 3.3	-0.123 ± 0.146	0.623	0.9987	57.4 ± 4.8	1.336	0.8663	58.5 ± 4.7	0.4867
PS/CH/55 °C	47.7 ± 0.4	0.043 ± 0.027	0.457	0.9998	47.5 ± 0.6	0.516	0.9558	47.8 ± 0.5	0.2398
PS/PVME (46.7/53.3, W/W)/CH/55 °C	33.0 ± 1.3	0.074 ± 0.135	0.426	0.9970	32.2 ± 1.2	0.566	0.6962	32.4 ± 1.1	0.0127
PVME/CH/55 °C	17.7 ± 0.3	0.034 ± 0.077	0.466	0.9995	17.9 ± 0.4	0.392	0.6168	18.0 ± 0.3	0.1690
PS/THF/20 °C	88.9 ± 0.4	0.178 ± 0.008	0.322	1.0000	88.1 ± 0.3	0.350	0.9973	88.0 ± 0.2	0.9957
PVME/THF/20 °C	31.8 ± 0.3	0.173 ± 0.024	0.327	0.9998	31.7 ± 0.5	0.338	0.9005	31.7 ± 0.4	0.7187
PS/PVME (49.8/50.2, W/W)/THF/20 °C	60.8 ± 0.2	0.165 ± 0.006	0.335	1.0000	60.3 ± 0.2	0.366	0.9984	60.4 ± 0.1	0.9942
(SB)2/TL/25 °C	80.6 ± 0.1	0.179 ± 0.003	0.321	1.0000	80.7 ± 0.2	0.327	0.9990	80.6 ± 0.2	0.9957

CONCLUSIONS

This article has demonstrated the advantages of the Wolf plot for the accurate and reproducible determination of intrinsic viscosities by means of numerous examples. The new method stems from the definition of intrinsic viscosity, and is free of any model assumptions. By plotting $\ln \eta_{rel}$ as a function of polymer concentration c , the initial slope of the dependence can be obtained to give the intrinsic viscosity $[\eta]$ directly. The experimental results evaluated from the viscosities of a variety of polymer solutions have indicated the high reliability of the new method. Moreover, avoiding the traditional zero-divided-by-zero type extrapolation increases the precision of the obtained $[\eta]$ naturally. It is therefore generally highly recommended to use the new method in order to obtain precise $[\eta]$ values. In the case of charged polymers and in the presence of extra salt or for low ionic strengths of the solvent, only this procedure yields unequivocal $[\eta]$ values. This specific feature is a prerequisite for the comparison of data reported in the literature for a particular system.

ACKNOWLEDGEMENT The support of the DAAD-K.C. Wong sponsoring the stay of X. Xiong in Germany is gratefully acknowledged.

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