Experimental Measurement of Diffusion in Aqueous Polyvinylpyrrolidone Solutions

Zoe A. Metaxiotou and Stavros G. Nychas
Chemical Engineering Dept., Aristotle University of Thessaloniki, 540 06 Thessaloniki, Greece

Diffusivities of aqueous dilute and semidilute polyvinylpyrrolidone solutions $M_w = 50{,}500$ and $M_w = 867{,}000$ were measured at 25°C. The measurements were performed by Taylor's hydrodynamic stability method and the dynamic light scattering (DLS) method. Taylor's method was compared to DLS and evaluated as an experimental technique to determine the molecular diffusivity in polymer solutions. The agreement between the two methods was very good with Taylor's method proving to be a reliable, simple, and inexpensive technique that provided diffusivity data with a maximum error of 5%.

Introduction

Molecular transport of mass is encountered often in polymer technology. In particular, molecular diffusivity data are of importance to a variety of polymer processing steps such as polymerization, polymer devolatilization, removal of residual monomer, and drying of solvents in polymer coatings industry. On the other hand, the mixing process at high Schmidt numbers, ($N_{Sc} = \nu/D$), is another area where diffusivity data are needed. The classical experimental techniques for the measurement of the diffusion coefficient in liquids are time-consuming in the case of polymer solutions, due to the extreme slowness of the diffusion process in such systems. Other faster experimental techniques based on flow processes have not been widely applied in polymeric systems mainly for concern of shear degradation. Dynamic light scattering (DLS) is an established and fast experimental technique; it is not, however, available in many laboratories mainly due to high investment cost associated with the technique. It is therefore justified to develop reliable and inexpensive methods in order to experimentally determine the diffusion coefficient in polymer/solvent systems.

Taylor (1953) in addition to his well-known dispersion technique proposed a second method (Taylor, 1954), which could be used to determine diffusion coefficients in liquids. This method is based on a hydrodynamic stability of a fluid inside a vertical capillary tube under conditions of inverse density gradient. It applies a stability criterion in order to obtain the mutual diffusion coefficient of the system. Taylor (1954) determined diffusivity values of the system $KMnO_4$ solution/water applying his hydrodynamic stability method and claimed that his data were in agreement with data reported by Furth and Ullmann (1927).

Anderson et al. (1978) used Taylor's method in order to determine the mutual diffusion coefficient for bovine serum albumin (BSA) and polystyrene latex particles as a function of concentration in aqueous potassium chloride solutions. Quinn et al. (1986) used the same technique to measure the diffusivity of small molecules and colloidal particles in aqueous solutions as a function of concentration and ionic strength. These works of Anderson et al. (1978) and Quinn et al. (1986) are the major contributions in developing an experimental method for the determination of the diffusion coefficient according to Taylor's hydrodynamic stability criterion. Metaxiotou and Nychas (1993) contacted a detailed visual investigation, applying close-up photography in order to study the motions of aqueous $KMnO_4$ solutions inside vertical capillaries under conditions of inverse density gradients. In addition, Taylor's criterion of neutral stability was applied in that study for the determination of the diffusion coefficient of aqueous $KMnO_4$ solutions as a function of concentration.

The accumulated experience of the cited, though limited, application of Taylor's technique shows that it provides a simple method of wide applicability in the topic of diffusivity in liquids. Moreover, the apparatus is simple and inexpensive while the numerical treatment of the data, in order to obtain the diffusion coefficient as a function of concentration, is very simple. This method, however, has not been used so far to measure the diffusion coefficient in polymer solutions. There

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Correspondence concerning this article should be addressed to S. G. Nychas.

it has the advantage of the low shear rates involved and therefore negligible shear degradation. In that sense Taylor's hydrodynamic stability method is attractive for shear sensitive polymer systems. All these characteristics of Taylor's method justify a further development and application of this technique to polymer solutions. The present work is a contribution towards this direction.

For that purpose, in the present work, polyvinylpyrrolidone (PVP) was chosen as a typical water soluble polymer in order to apply Taylor's method; then compare it to another independent method (DLS) and establish possible limitations in the application of the technique to polymer solutions. In this study the binary diffusion coefficient of aqueous PVP solutions of two different molecular weights was measured as a function of concentration over a region covering very dilute to semidilute solutions. These PVP solutions were measured with both Taylor's hydrodynamic stability method and DLS. Based on the diffusivity data obtained by these two independent techniques, Taylor's method was evaluated. In this comparative evaluation, DLS was considered as an established, accurate and fast method with a theoretical foundation of wide acceptance at least at low polymer volume fractions (Pecora, 1985). In addition, the present work provides new and complete diffusivity data for the system PVP/water for two molecular weights ($M_w = 50{,}500$ and $M_w = 867{,}000$) over a wide concentration range.

Principles of experimental techniques

The experimental setup, used in Taylor's hydrodynamic stability method, consists of a vertical capillary tube filled with liquid of density ρ_o, closed at the bottom; the capillary is connected at the top to a reservoir containing a solution of the same liquid and of density greater than ρ_o. Due to the density difference between the two fluids, a convective downward current of the heavier solution is induced. At the same time, a rising current of the displaced solvent in the capillary is moving upwards. These currents stop when the vertical density gradient does not exceed the following critical value obtained by Taylor (1954):

$$\frac{d\rho}{dz} = 67.94\,\frac{\eta D}{g b^4} \tag{1}$$

here, g is the gravitational acceleration, b is the radius of the tube, η is the viscosity of the fluid, and D is the diffusivity of the solute producing the variation in ρ. Taylor's stability method provides a simple way of measuring a fluid's ηD product, provided that there is a way to quantitatively measure the density gradient $d\rho/dz$ (Eq. 1). In this way Taylor's analysis provides a method for the determination of the diffusivity D.

The method of DLS during the last two decades has proven to be an accurate, reliable and very fast technique for the determination of the diffusivity of macromolecules in solution. The method, extensively reviewed in the literature (Berne and Pecora, 1976; Pecora, 1985; Burchard, 1985) is based on the analysis of the Doppler broadened spectrum of the scattered light intensity. This Doppler broadening is caused by the continuous motion of the molecules in the sample due to the process of diffusion. By applying the autocorrelation technique on the measured scattered light intensity, the diffusion coefficient of the system under consideration can be obtained.

Experimental and Data Analysis

Taylor's hydrodynamic stability method

The experimental apparatus for the measurement of the diffusion coefficient of the system PVP/water is shown in Figure 1. It consisted of a long glass capillary of known diameter, closed at the bottom, with a system of a removable rubber membrane. This system permitted the filling of the capillary with a syringe without introducing air bubbles in it. This was accomplished by inverting the capillary into a vial with distilled water and drawing solvent into an empty syringe through the membrane. The capillary was then connected to a reservoir in a vertical position in such a way that its free upper surface was approximately 1–2 mm higher from the bottom of the reservoir. It was found that this configuration, combined with careful filling of the reservoir, minimized the convective currents induced during the initial contact of the two fluids. The reservoir was always filled with the same volume of PVP solution (approximately 120 cm^3), which was large enough to ensure that no significant dilution effects occurred due to the solvent displacement from the capillary. The volume of solution above the upper end of the capillary prevented the propagation of disturbances from the air above the solution into the capillary. Capillaries of 0.08 cm, 0.10 cm, 0.14 cm, and 0.20 cm in dia. and 100 cm long, purchased from Specialty Glass Products, Willow Grove, PA were used for the experiments. For these capillary dimensions, the length to diameter ratio, $L/(2b)$, varied from 500 to 1,250. The tolerance in dia., given by the manufacturer, was ±0.3%, ±0.2%, ±0.2%, and ±0.1% for the capillaries used, respectively. Each run involved several capillary/reservoir systems operating simul-

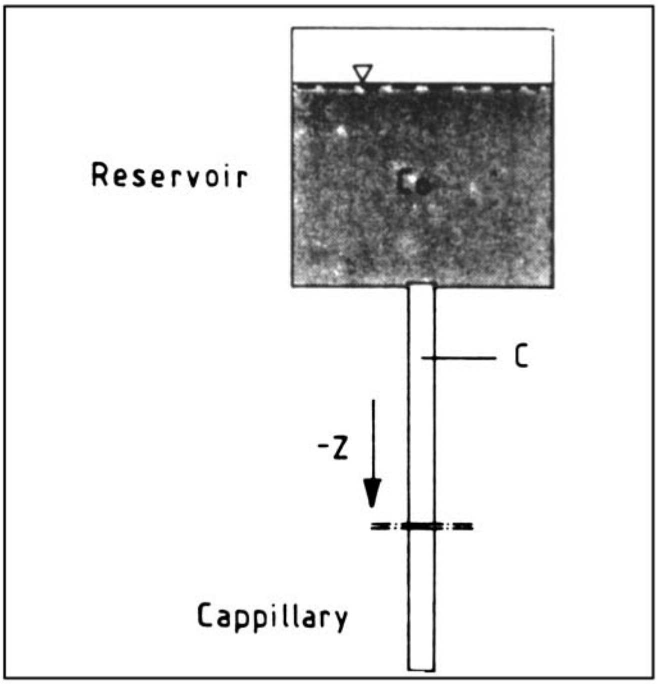

Figure 1. Experimental apparatus of Taylor's hydrodynamic stability method.

taneously. The capillaries were housed in a box (air bath) where the temperature was kept constant to within ±0.5°C by means of two 100 W lamps and a temperature controller. In this way, convection currents, which otherwise could cause the capillary to vibrate, were eliminated. The experimental data were reproduced up to four times. Quinn et al. (1986) proposed a procedure to evaluate diffusivity on the basis of Taylor's method. They used Eq. 1 in the following form:

$$D_o = \frac{\alpha g b^4 (C_o)^2}{2(67.94)\eta L C} \tag{2}$$

where C_o is the polymer concentration in the reservoir, η is the viscosity of the polymer solution, α is a parameter which gives the relation between the density and the concentration of the solution, and C is the mean polymer concentration in the capillary. In deriving the above relation, Quinn et al. (1986) assumed that all physical properties were independent of solute concentration. This assumption, however, is not valid in the case of the system PVP/H_2O. Diffusivity data obtained with DLS (see next section), as well as viscosity measurements showed that both these properties of aqueous PVP solutions are not independent of concentration. In fact, the diffusivity and the viscosity dependencies on concentration could be approximated by the following linear functions for both molecular weights:

$$D = D_o(1 + k_D C_o) \tag{3}$$

$$\eta = \eta_o(1 + mC_o) \tag{4}$$

In Eq. 3, D_o and k_D for the purpose of the present work were determined from DLS diffusivity data (see next section). The constants η_o and m in Eq. 4 were obtained from viscosity measurements. During these measurements, the viscosities of aqueous PVP solutions of concentrations between 0.05% and 4% for $M_w = 50{,}500$ and between 0.05% and 0.40% for $M_w = 867{,}000$ were obtained at 25°C. All measurements were performed using a Cannon-Fenske capillary viscometer thermostated in a water bath and are given in Table 1. The maximum error in the measured specific viscosity of the polymer solutions, obtained for the lower concentration examined, was 1.7%. Quinn et al. (1986) extended the stability criterion (Eq. 1) in order to include concentration dependencies in the form of Eqs. 3 and 4 and arrived at the following expression:

$$\frac{1}{m - k_D} \ln \frac{(D/D_o)^{1/k_D}}{(\eta/\eta_o)^{1/m}} = \left[\frac{(67.94)L}{\alpha g b^4}\right] D_o \eta_o C \tag{5}$$

Equation 5 constituted the working relationship for our calculations of the diffusivity D for both polymer molecular weights along the entire concentration region, examined.

In order to obtain the values of the parameter α in Eq. 5, the density of PVP solutions was measured as a function of solute concentration using a digital densimeter (Anton Paar, DMA 60). The concentration regions examined were between 0.05% and 2.5% for $M_w = 50{,}500$ and 0.05% and 0.60% for $M_w = 867{,}000$, respectively. All density measurements were performed at 25°C and their precision was $\pm 2 \times 10^{-6}$ g·cm^{-3}. In this way the values of α obtained were 1.935×10^{-3} and 2.109×10^{-3} for $M_w = 50{,}500$ and $M_w = 867{,}000$, respectively.

Table 1. Viscosity of Aqueous PVP Solutions as a Function of Concentration at 25°C

$M_w = 50{,}500$		$M_w = 867{,}000$	
Conc. (g/100 cm^3)	Vis. (cSt)	Conc. (g/100 cm^3)	Vis. (cSt)
0.05	0.922	0.05	0.981
0.10	0.934	0.10	1.063
0.15	0.948	0.15	1.149
0.20	0.958	0.20	1.236
0.25	0.970	0.25	1.321
0.30	0.984	0.30	1.424
0.40	1.008	0.35	1.526
0.60	1.060	0.40	1.644
0.80	1.113		
1.40	1.285		
2.00	1.475		
2.50	1.653		
3.00	1.839		
3.50	2.035		
4.00	2.246		

After approximately 100 h from the initial contact between the polymer solution in the reservoir and the water in the tube, the capillary was disconnected from the reservoir. The estimation of this experimental run time was based on the calculations of Quinn et al. (1986), who suggested the following relation which gives in a nondimensional form the time, t_c, required to reach stable conditions:

$$\frac{t_c D}{b^2} \approx 25 \tag{6}$$

The mean concentration, C, of PVP in the capillary was determined by means of a VARIAN high performance liquid chromatography (HPLC) system using a size exclusion type TSK column. In order to obtain C a series of PVP solutions of known concentrations were prepared for each experiment. A calibration curve obtained from these solutions permitted the determination of the unknown C by linear interpolation. Once C was obtained, D could be determined according to Eq. 5 with D_o, η_o, η, m and k_D determined experimentally as mentioned before. In the present study, the experiments with $M_w = 50{,}500$ covered a concentration range from very dilute (0.20%) to semidilute (8%) solutions. For the samples of $M_w = 867{,}000$, the experiments covered the dilute region up to 0.55% solutions.

Wooding (1960) discussing the instability of a viscous fluid in a vertical Hele-Shaw cell commended the possibility of the heavier fluid to penetrate inside the tube further than predicted by Taylor's analysis. This phenomenon, which he called "overshooting," characterizes a fluid motion which can never lead to a situation of neutral stability. It is an undesirable phenomenon when the objective is to measure the molecular diffusivity and/or establish a linear concentration gradient in liquids, and it was also observed by Quinn et al. (1986). Overshooting is easily detectable in the case of colored diffusing solutes ($KMnO_4$/water) from a penetration length vs. time plot as shown by Metaxiotou and Nychas (1993). Such a plot in a case of overshooting is characterized by the absence of a plateau region and the almost constant slope in the curve. In cases of colorless fluids, as in the present work, the occurrence of this phenomenon cannot be visually detected. Overshooting can be minimized, however, by introducing the PVP solution very carefully in the reservoir and by performing multiple runs under identical conditions. In this way reproducible values of D for each molecular weight and capillary radius were obtained. All solutions were prepared using distilled, deionized water and PVP with molecular weights purchased from BDH, Ltd. equal to 50,500 and 867,000, respectively. Low angle light scattering (LALLS) was used in order to evaluate the above weight average molecular weights, M_w, of the two polymers. Both polymers were used without further purification with a maximum residual monomer content of 0.8%. All polymer solutions were prepared gravimetrically and usually one day before the actual experiment.

Dynamic Light Scattering

Aqueous PVP solutions were prepared gravimetrically one day before measurement to make sure that the polymer was completely dissolved; nanopure water was used for all solution preparations. The homogeneous solutions were then filtered through a 0.22 μm Millipore filter directly into dust free scattering cells. The concentration regions examined were up to 12% for $M_w = 50{,}500$ and up to 2.4% for $M_w = 867{,}000$, respectively. The refractive index for each sample was measured with a refractometer in order to calculate the scattering vector q. The time correlation function of the scattered light intensity (at 25°C) was measured at a scattering angle of $\theta = 90°$. An Ar^+ laser (Spectra Physics 2020) operating at 488 nm with a power of 100 mW was used as the light source. The correlation function $G(t)$ over nine decades in time was measured with a 248-channel, multi-τ digital correlator (ALV 5000). The data were fitted with a stretched exponential function of the form $G(t) - 1 = \exp(-t/\tau^*)^{\beta}$, where the distribution parameter β was approximately 0.85 for $M_w = 50{,}500$ and 0.91 for $M_w = 867{,}000$. All measured correlation functions were single modal. The relaxation time τ^* was alternatively calculated using the method of cumulants from the first cumulant. The translational diffusion coefficient D at a certain concentration is related to the τ^* according to:

$$D = 1/(q^2\tau^*) \tag{7}$$

where q is the scattering vector defined as:

$$q = (4\pi n/\lambda)\sin\theta/2 \tag{8}$$

Here, n is the solution refractive index, λ is the wavelength of light, and θ is the scattering angle.

Results and Discussion

The experimental results for the diffusion coefficient of PVP solutions, as obtained by Taylor's method, are presented in Tables 2 and 3 for $M_w = 50{,}500$ and $M_w = 867{,}000$, respectively. These data are plotted in Figure 2 where the initial reservoir concentration, C_o, is given in a nondimensional form normalized with the overlapping concentration C^*. This concentration denotes a solution state where the polymer coils start to overlap. A reliable estimate of this characteristic concentration is $C^* \approx 1/[\eta]$ where $[\eta]$ is the value of the intrinsic viscosity at infinite dilution (De Gennes, 1990). From our viscosity measurements, C^* was determined to be 3.84 g/100 cm³ for $M_w = 50{,}500$ and 0.63 g/100 cm³ for $M_w = 867{,}000$.

Table 2. Diffusion Coefficient of Aqueous PVP Solutions, ($M_w = 50{,}500$), as Determined with Taylor's Hydrodynamic Stability Method at 25°C

C_o (g/100 cm³)	$10^7 D$ (cm²/s)	C_o (g/100 cm³)	$10^7 D$ (cm²/s)
$b = 0.04$ cm		$b = 0.05$ cm	
2.0	4.60	2.0	4.61
3.0	4.94	3.0	4.99
5.0	5.88	5.0	5.89
6.0	6.32	6.0	6.29
8.0	7.41	8.0	6.30
$b = 0.07$ cm		$b = 0.10$ cm	
0.4	4.03	0.2	3.97
0.6	4.10	0.4	4.03
0.8	4.16	0.6	4.09
1.0	4.23	0.7	4.12
1.2	4.30		
1.4	4.38		
1.6	4.45		
1.8	4.52		
2.0	4.60		

The diffusivity data in Figure 2 show clearly that there is no dependence on capillary diameter. This result is consistent with the observations of Anderson et al. (1978) and Quinn et al. (1986) and provides confidence in the reliability of Taylor's method. The duration t for all experiments was approx. 100 h, as mentioned before. For part of the measurements, this time t is an overestimation of the optimized time t_c required by the fluid to reach stable conditions. The excess time $(t - t_c)$ varies between 20 to 70 h depending on the capillary diameter. During that time any concentration changes inside the capillary are attributed to diffusion. This process, however, is very slow in systems of high Schmidt numbers ($N_{Sc} = \nu/D$), as in the present study. An estimation of the error due to the excess time was made in the following way. A visualization of the motions was carried out by coloring the PVP solutions with small amounts of Congo red ($D \approx 1.6 \times 10^{-6}$ cm²/s, Fürth and Ullmann, 1927). A number of experimental runs were performed, and it was deduced that typical polymer penetration

Table 3. Diffusion Coefficient of Aqueous PVP Solutions, ($M_w = 867{,}000$), as Determined with Taylor's Hydrodynamic Stability Method at 25°C

C_o (g/100 cm³)	$10^7 D$ (cm²/s)	C_o (g/100 cm³)	$10^7 D$ (cm²/s)
$b = 0.07$ cm		$b = 0.10$ cm	
0.15	1.05	0.05	0.97
0.20	1.10	0.10	1.01
0.25	1.14	0.15	1.05
0.30	1.20	0.20	1.09
0.35	1.24	0.25	1.14
0.40	1.28	0.30	1.18
0.45	1.35		
0.50	1.40		
0.55	1.45		

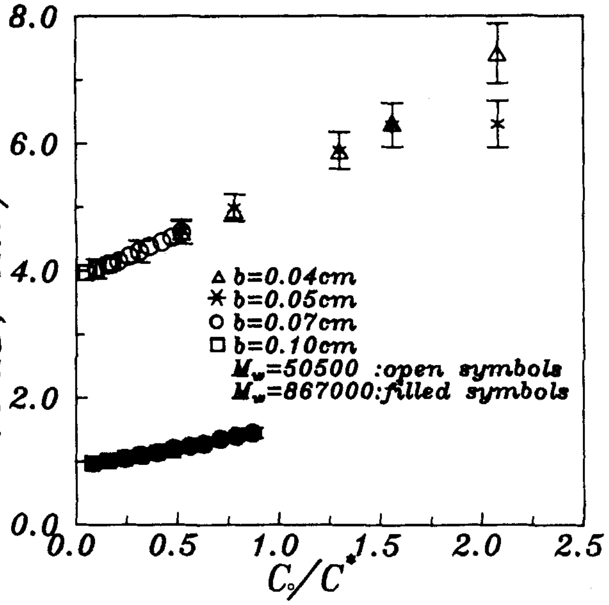

Figure 2. Experimental diffusivity values of aqueous PVP solutions obtained with Taylor's hydrodynamic stability method.

Table 4. Diffusion Coefficients of Aqueous PVP Solutions, $M_w = 50{,}500$ and $M_w = 867{,}000$, as determined by DLS at 25°C

$M_w = 50{,}500$		$M_w = 867{,}000$	
C_o (g/100 cm^3)	$10^7 \times D$ (cm^2/s)	C_o (g/100/cm^3)	$10^7 \times D$ (cm^2/s)
0.4	3.225	0.05	0.983
0.6	3.561	0.10	1.007
0.8	4.050	0.15	1.049
1.0	4.065	0.20	1.090
1.2	4.268	0.25	1.149
1.4	4.282	0.30	1.207
1.6	4.483	0.35	1.232
1.8	4.633	0.40	1.283
2.0	4.749	0.45	1.318
2.5	4.895	0.50	1.410
3.0	5.142	0.55	1.444
3.5	5.389	0.65	1.554
4.0	5.585	0.85	1.779
4.5	5.864	1.00	1.932
7.0	6.651	1.20	2.117
9.0	7.669	1.40	2.302
12.0	8.317	1.70	2.622
		2.00	2.806
		2.40	3.192

lengths were of the order of 50–80 cm. During the excess time, the maximum variation of the penetration length due to axial diffusion ($D \approx 5 \times 10^{-7}$ cm^2/s) was of the order 0.35 cm. This would introduce a maximum error in the D value of the order of 1%. The fact that D values, obtained under conditions of optimized run times ($b = 0.07$ cm) and long excess times ($b = 0.04$ cm and $b = 0.05$ cm), were practically identical verifies this estimation. In Figure 2 representative error bars are drawn through data points. In order to estimate the error encountered in the calculated values of D, a standard error propagation analysis procedure was applied on Eq. 5 (Miller and Miller, 1988). The main error contributions to the total error of D came from the least-square fit parameters D_o, k_D, m, η_o, and the mean concentration C. The relative standard deviations (RSD) of the first four parameters are 3%, 8%, 5%, and 3%, respectively, for $M_w = 50{,}500$, and 2.5%, 3%, 7%, and 3% for $M_w = 867{,}000$. Concerning the error in C this was estimated to be of the order of 5% for both molecular weights. The larger total errors obtained with semidilute solutions of $M_w = 50{,}500$ (Figure 2) are attributed to the less satisfactory fit of a linear relationship to the viscosity data at this high concentration region.

The diffusion coefficients for the system PVP/H_2O, measured with DLS for $M_w = 50{,}500$ and $M_w = 867{,}000$, are presented in Table 4 and shown in Figure 3. For very dilute solutions ($C_o < 0.5C^*$), a change in the slope of the curve corresponding to $M_w = 50{,}500$ is observed. This behavior can be attributed to the polydispersity of these samples. At low M_w, namely, the existence of high molecular weight chains gives rise to an apparent lower diffusion coefficient, as shown in Figure 3. As the concentration becomes higher, however, this effect of polydispersity diminishes. The second cumulant in the cumulant expansion $K_2 = \langle (\Gamma - \langle \Gamma \rangle)^2 \rangle$, where $\langle \Gamma \rangle = 1/\tau^*$ is the average relaxation rate, is a measure of the polydispersity of the sample (Pecora, 1985; Koppel, 1972). This second cumulant was of the order of 0.15 for $M_w = 50{,}500$ and of the order of 0.18 for $M_w = 867{,}000$, which indicates polydisperse samples. The sample polydispersity was also verified by the value of the distribution parameter β, which in the case of a monodisperse system is equal to 1. From Figure 3, the infinite dilution diffusivity value D_o and the slope k_D were obtained from least-square linear fits to the data. A similar approach was applied to the data in Figure 2 in order to obtain the corresponding D_o and k_D values from Taylor's method. These results are presented in Table 5 where data for a system of

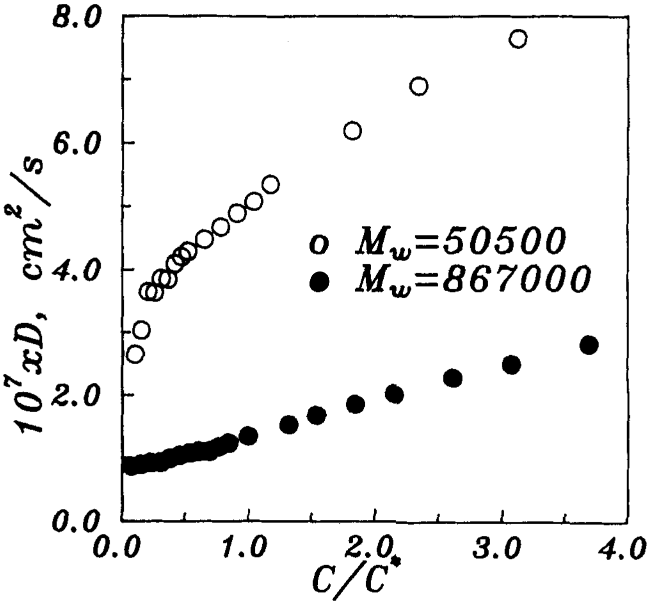

Figure 3. Experimental diffusivity values of aqueous PVP solutions obtained with DLS.

Table 5. D_o and k_D Values for Aqueous PVP Solutions Obtained with Taylor's Method and DLS

	$10^7\ D_o$ (cm^2/s)			k_D (10^2 cm^3/s)		
M_w	Taylor	DLS	PS/THF*	Taylor	DLS	PS/THF*
50,500	3.79	3.88		0.114	0.102	
867,000	0.901	0.912		0.974	0.952	
51,000			7.65			0.16
860,000			1.59			1.36

*Comparison with corresponding DLS data for the system PS/THF.

comparable M_w in good solvent (polystyrene in tetrahydrofuran) measured with DLS (Mandema and Zeldenrust, 1977) are also included. Concerning the data in Table 5, it should be mentioned that the D_o and k_D values obtained with DLS have been calculated from least-square fits over more extended concentration ranges than the corresponding Taylor's values. It is evident from the results in Table 5 that the agreement between Taylor's method and DLS is very good. These results of D_o and k_D are also close to the corresponding data for the PS/THF system. The data in Table 5 verify experimentally the extention of Taylor's criterion (Eq. 5) proposed by Quinn et al. (1986). Comparison of our experimental results with other diffusivity data for the PVP/H_2O system obtained with DLS (Burchard and Eisele, 1984) can be done only on a qualitative basis. These authors plot the diffusion coefficient for an intermediate PVP molecular weight ($M_w = 560{,}000$) against C/C^* in a double logarithmic plot. Our data when plotted in the same way show a similar concentration dependence.

Concerning the comparison between Taylor's method and DLS, some important aspects should be addressed. Taylor's method yields the macroscopic coefficient appearing in Fick's law. The measured quantity D is an integral average over the concentration range of the experiment. The DLS technique on the other hand observes the growth and decay of microscopic concentration fluctuations in systems, which macroscopically are gradientless. In the so-called hydrodynamic limit where such fluctuations are observed over long distances compared to the intermolecular spacing and over long times compared to their relaxation times, DLS is expected to yield the same D as measured by conventional boundary spreading techniques (Pecora, 1985). This is true at least for low concentrations. In the case of a polydisperse polymer both Taylor and DLS diffusivities are averages over all the molecular sizes of the chains. DLS diffusivities are z-averages. During a Taylor experiment, however, the smaller molecules diffuse inside the capillary faster than the larger ones. As a consequence, Taylor diffusivities do not weight the larger molecules to the same extent as DLS does. This could provide an explanation for the deviation between the two methods for the $M_w = 50{,}500$ at low concentrations. Even if a direct comparison between Taylor's method and DLS is restricted due to the aforementioned differences, it is valuable to confirm on the same system the identity of the quantity measured by these two methods. Such comparisons between conventional techniques and DLS have previously been made and both agreement (Anderson et al., 1978) and discrepancies (Phillies et al., 1976) have been observed.

Finally, based on our experience, Taylor's method can be applied to dilute and semidilute polymer solutions provided that accurate expressions for the concentration dependences of D and η are known. For higher concentrations, however, one should consider practical limitations such as the use of longer capillaries and/or smaller capillary diameters.

Conclusions

The results of the present study can be summarized as follows:

- Taylor's hydrodynamic stability method is an inexpensive, reliable, and simple experimental technique for the determination of the binary diffusion coefficient in polymer solutions. Using that method, D values with a maximum experimental error of the order of 5% were obtained in dilute and semidilute solutions.
- The diffusion coefficients of aqueous PVP solutions obtained with Taylor's method agree with the diffusivity values measured with DLS for the same solutions to within 3% for $M_w = 50{,}500$ and 1% for $M_w = 867{,}000$. This consistency in the diffusivity data confirms that the two independent techniques measure the same diffusion coefficient.
- The results presented in this work experimentally verify the Quinn et al. extention of Taylor's criterion to conditions of concentration dependent diffusivities and viscosities.

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Notation

b = capillary radius, cm
C = mean solute concentration, g/100 cm^3
C^* = polymer overlapping concentration, g/100 cm^3
C_o = solution initial concentration, g/100 cm^3
D = solute diffusion coefficient, cm^2/s
D_o = diffusion coefficient at infinite dilution, cm^2/s
g = gravitational acceleration, cm/s^2
$G(t)$ = correlation function
k_D = parameter, Eq. 3
K_2 = second cumulant, s^{-2}
L = capillary length, cm
m = constant, Eq. 4
q = scattering vector, cm^{-1}
t = time, s
t_c = time required for stable conditions inside the capillary, s
z = distance along capillary axis, cm

Greek letters

α = parameter, Eq. 2
β = distribution parameter
$\langle\Gamma\rangle$ = average relaxation rate, s^{-1}
η = solution viscosity, g/cm·s
η_o = solvent viscosity, g/cm·s
$[\eta]$ = solution intrinsic viscosity, g/cm^3
λ = wave length, cm
ν = kinematic viscosity, cm^2/s
ρ = solution density, g/cm^3
ρ_o = solvent density, g/cm^3
τ^* = relaxation time, s

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