Use of Taylor Dispersion for the Measurement of Probe Diffusion in Polymer Solutions

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Diffusion of small molecules in liquid systems containing polymers is important in many processes including membrane permeation, the devolatilization of polymers, the drying of coatings, and diffusion-controlled polymerization. Unfortunately, diffusion data in polymer solutions are relatively limited (Zielinski and Duda, 1992), in part because many techniques involved in diffusion measurements are time consuming. Recently there has been renewed interest in methods that allow for rapid and inexpensive measurements of diffusion coefficients in small molecule and polymer solutions (Al-Naafa and Selim, 1994; Bello et al., 1994; Burkey et al., 1984; Huggenberger et al., 1980; Metaxiotou and Nychas, 1995). Here we report on an application of an often overlooked technique, originally proposed for small molecule solutions, for measuring diffusion coefficients of small molecules and polymers in polymer solutions. This rapid and relatively inexpensive technique is based on the dispersion of a solute in a liquid undergoing laminar tube flow, and is commonly referred to as Taylor dispersion.

The theory was first discussed by Taylor (1953, 1954), and later by Aris (1956), and was applied by Ouano (1972) who demonstrated that the solute diffusion coefficient in a two-component system can be determined from the mean and variance of the solute concentration profile as it exits the tube. The technique was further developed by Pratt and Wakeham (1974) and Grushka and Kikta (1974). A number of restrictions and corrections to the analysis relating to sample injection, detector volume, tube uniformity, connecting volumes, and tube coiling can be applied, as reviewed by Alizadeh et al. (1980). Recently, the theory has been extended to systems of three or more components by Price (1988) and Leaist (1990). While the Taylor dispersion technique has been used previously to measure diffusion in dilute solutions of polymers such as polymethylenes (Chen and Chen, 1985), polystyrenes (Barooah et al., 1985, 1986; Sun et al., 1987), and dextrans and dendrimers (Boggs, 1994), the development in this work has extended the applicability of this technique so as to make measurements of tracer diffusion coefficients of polymers and small molecules in more concentrated polymer solutions—in some cases in solutions of at least 400 g/L polymer concentration.

Taylor has shown that the mean concentration of solute at a time t after a δ-pulse injection of fluid into a laminarly flowing stream can be expressed as

$$C(t) = \frac{m}{\pi a^2 (2\pi)^{1/2} \bar{U} (2Kt/\bar{U}^2)^{1/2}} \exp\left[- \frac{(t-\bar{t})^2}{2(2Kt/\bar{U}^2)} \right] \tag{1}$$

where m is the mass of the solute (g), a is the tube radius (cm), $\bar{t}$ is the dispersion time (min), $\bar{U}$ is the average velocity (cm/m), and K is the dispersion coefficient. Provided that Taylor's condition $\bar{t} \gg a^2/(3.8)^2\,\mathfrak{D}$ is met, the dispersion coefficient can be expressed as

$$K = \mathfrak{D} + a^2\bar{U}^2/48\,\mathfrak{D}. \tag{2}$$

where $\mathfrak{D}$ is the diffusion coefficient (cm^2/s). Equation 1 is a Gaussian curve with mean $\bar{t}$ and variance σ^2 of $2Kt/\bar{U}^2$. Thus, for long dispersion times, and for most experimental conditions in which $\mathfrak{D}$ is on the order of 10^{-5} cm^2/s, $\mathfrak{D}$ can be expressed as (Levenspiel and Smith, 1957)

$$\mathfrak{D} = \frac{a^2\bar{t}}{24\sigma^2} \tag{3}$$

For systems with $\mathfrak{D} < 10^{-6}$ cm^2/s, it is necessary to consider higher order terms of Eq. 2. Thus, the working equation for the diffusion coefficient becomes (Pratt and Wakeham, 1975)

$$\mathfrak{D} = \frac{a^2\bar{t}}{48\sigma^2}\left[1 + \left(1 + \frac{4\sigma^2}{\bar{t}^2}\right)^{1/2}\right] \tag{4}$$

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For Taylor's condition to be met, slow flows in long tubes and/or narrow bore capillaries are required. Bello et al. (1994) approached the problem with 50–100-μm ID capillaries commonly used for capillary electrophoresis. With a 1-m-long capillary, experiments could be performed very rapidly—in most cases less than 1 min. However, the method suffered from chemically specific solute-wall interactions with the use of uncoated capillaries due to the extremely narrow tube dimensions. The more common method is to employ 0.5–1.0-mm ID tubing often used for high-pressure liquid chromatography, with a tube length of 10–50 m. Due to physical constraints the tubing is usually wound into a coil or helix. As Eqs. 1–4 were derived for straight tubes, and as tube curvature can create secondary flows, use of Eqs. 3 and 4 is limited to conditions in which $Dn^2Sc < 20$. Otherwise, values of the measured diffusivity are erroneously high (Janssen, 1976). Here, the Dean number (Dn) is $\lambda^{-0.5}Re$, the Reynolds number (Re) is $2\bar{U}a\rho/\mu$, λ is the ratio of the coil radius to the tube radius, and the Schmidt (Sc) number is $\mu/(\rho\mathcal{D})$. The effects of curvature on measurements of $\mathcal{D}$ are minimal for most liquids when low flow rates are used. However, for measures of polymer or small molecule diffusion in polymer solutions, the lower value of $\mathcal{D}$ (and higher Sc number) exacerbates the problem. In order to minimize curvature effects in this study, we chose to use a unique "square-shaped" tube geometry with only four wide bends.

Experimental Studies

The apparatus consisted of a solvent reservoir, a Waters 501 HPLC pump, upstream connecting tubing, an Anspec 720 autosampler with a Valco pneumatic injector, the dispersion tube, an in-line-filter and union, a Waters 484 tunable UV absorbance detector, downstream connecting tubing with a volume of 100 μL, another union, and a Waters 410 differential refractometer. In order to illustrate the effect of tube curvature, two dispersion tubes were used. The first, a coiled tube, had tube dimensions similar to those used by Pratt and Wakeham (1975). The stainless steel tube (Alltech 3000) was 30.5 m long and had an internal radius a of 0.405 ± 0.005 mm, determined by weighing the amount of water required to fill a given length of tubing. The coil radius R_c was 0.115 m. The entire tube was placed in a water bath with temperature regulated to ±0.1°C by a Haake 42A recirculating pump and controller. The second tube had the same internal radius and length as the first, but was unwound so as to follow the perimeter of a 58-m^2 lab space. Except for bends at the corners of the room (6 m in length), the trajectory of the tube was primarily straight. The tube temperature was maintained by encasing it in 3/8-in. (9.5-mm) ID polybutylene tubing through which water at ±0.5°C of the set temperature was flowing. The pump was capable of flow rates from 0.1 to 10 mL/min in increments of 0.1 mL/min, and had a built-in pulse dampener. Except where dispersion time was an experimental parameter, the flow rate was set at 0.3 mL/min (Re of about 15 and a dispersion time of about 50 min). The injection volume was 20 μL, about 1/1,000 the total volume of the tube. The probe concentration in the injected phase was 2 g/L; with use of a dilute probe concentration, $\mathcal{D}$ can be defined as a tracer diffusion coefficient. For studies of ternary probe diffusion in polymer solutions, the mobile phase contained polymer and solvent while the injected phase contained polymer, solvent, and probe.

The detector output was collected by a Waters SIM data acquisition module and stored for later analysis. In ternary systems use of the differential refractometer detector was problematic because signal due to the concentration of probe as well as any differences in polymer concentration between the mobile phase and injected phase were detected. The UV absorbance detector did not suffer from this problem since it was tuned to a wavelength where probe absorbed and polymer did not. In addition, the differential refractometer had more baseline drift than the UV detector. Therefore, the differential refractometer was used only for detection of non-UV-absorbing molecules in binary systems. Chromatograms were fit by nonlinear regression to the following:

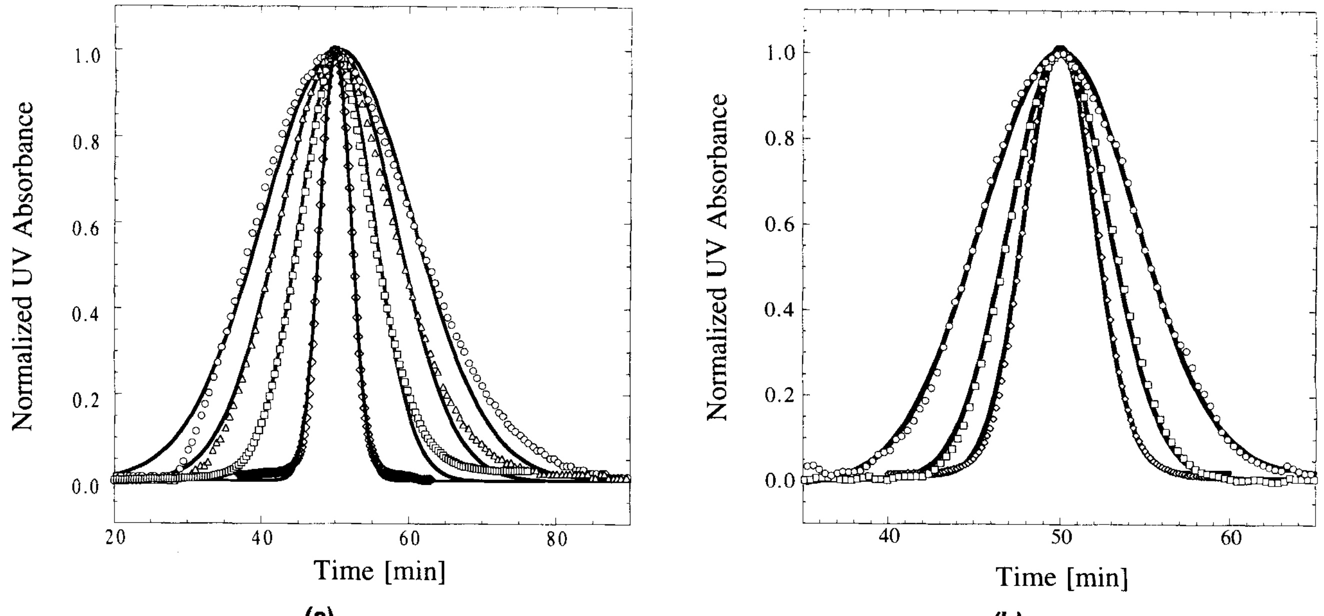
$$Y = A + B\exp\left[\frac{(t-\bar{t})^2}{2\sigma^2}\right] + \epsilon t \qquad (5)$$

where Y is the detector response, A, B, $\bar{t}$, σ^2, and ϵ are fitted parameters. Generally, baseline drift was negligible and $\epsilon = 0$. Using the fitted values of $\bar{t}$ and σ^2, the diffusion coefficients were calculated from Eq. 4. At a value of $\mathcal{D} = 3.9 \times 10^{-7}$ cm^2/s, Eq. 3 underestimates $\mathcal{D}$ by 6%, while at values of $\mathcal{D} > 1.5 \times 10^{-6}$ cm^2/s the difference between the two equations is less than 1%.

Solvents and small molecules (Aldrich) were used as received. Polystyrene (PS) ($\bar{M}_n = 3{,}500$; $\bar{M}_w/\bar{M}_n = 1.05$) was synthesized anionically using s-butyllithium as initiator in cyclohexane. The molecular weight of polymer in the mobile phase was chosen to be low so as to minimize the bulk solution viscosity (facilitating transport through the pump and tubing) and to maintain Newtonian flow. (Although the glass transition temperature of bulk PS is a function of molecular weight at this value, phosphorescence quenching studies have shown the overall free volume of the polymer solution at concentrations up to 400 g/L to be, within experimental error, relatively independent of molecular weight down to 4,000 g/mol (Yu and Torkelson, 1988).) Anthracene-terminally-end-labeled polystyrene (PS-A) was synthesized by reaction of living polystyryl anion with 9-(chloromethyl)anthracene in cyclohexane (Gebert et al., 1992). Molecular weights were determined by gel permeation chromatography.

Results and Discussion

In order to assess the applicability of Taylor dispersion for measuring small molecule and polymer diffusion in polymer solutions, values of $\mathcal{D}$ were first measured for anthracene and a series of PS-A molecules in cyclohexane at 25°C, using the "square-shaped" tubing. Figure 1a shows the UV absorbance detector output at 365 nm, normalized for the sake of clarity. The profiles are Gaussian-shaped and are fit to Eq. 5 with a correlation coefficient of $r^2 > 0.996$. The 50k PS-A profile, which is slightly non-Gaussian due to the low $\mathcal{D}$ value, has an $r^2 = 0.992$; skewness can result when longitudinal mixing is significant (Levenspiel and Smith, 1957). The figure demonstrates an inverse relationship between $\mathcal{D}$ (listed in Table 1) and the variance σ^2 expected of Taylor dispersion. Table 1 illustrates that as $\bar{M}_w$ for PS-A increases



(a)

(b)

Figure 1. Normalized UV absorbance detector output.

(a) Measuring diffusion of 50 K PS-A (○), 17K PS-A (△), 10K PS-A (□), and anthracene (◇) in cyclohexane at 25°C; (b) measuring diffusion of anthracene in solutions of 0 g/L PS (◇), 300 g/L PS (□), and 400 g/L PS (○) in THF at 25°C. Solid curves represent fits to Eq. 5.

from 10,000 to 88,000 g/mol, $\mathfrak{D}$ decreases by 72% to a value of 3.9×10^{-7} cm^2/s, to our knowledge the lowest value of $\mathfrak{D}$ reportedly measured by Taylor dispersion. This demonstrates the applicability of Taylor dispersion to the study of diffusion of moderately-sized polymers in dilute solution.

The accuracy of the diffusion measurements obtained via Taylor dispersion with this "square-shaped" tubing may be verified in two ways. First, values of $\mathfrak{D}$ were measured for several solutes at 25°C and compared with values from the literature. Table 1 summarizes the results in which the values of $\mathfrak{D}$ from this study represent averages of between three and ten experimental trials, with reproducibility within 2%. The agreement with literature values is very good, especially considering that most of the referenced values were obtained with a diaphragm cell rather than Taylor dispersion; the average accuracy, as compared to referenced values, is within 2%. A notable exception is the value for methyl red where the referenced value was measured using forced Rayleigh scattering by Landry et al. (1988). Second, it is known that for monodisperse polymers in dilute solution in a θ-solvent $\mathfrak{D} \sim M^{-0.50}$ where M is molecular weight (Flory, 1953); the limited data from this study reveal that $\mathfrak{D} \sim M^{-0.51}$, in agreement with expectations.

Figure 1b shows similar absorbance output from the Taylor dispersion measurements of anthracene diffusion as a function of PS concentration in tetrahydrofuran (THF). All three

Table 1. Diffusion Coefficients of Solutes in Various Solvents at 25°C

Solute	Solvent	$\mathfrak{D}\times10^5$ cm^2/s	Lit. Value	Reference
Ethanol	Water	1.17	1.24	Hammond and Stokes (1953)
L-phenylalanine	Water	0.717	0.705	Bello et al. (1994)
Sucrose	Water	0.514	0.520	Cussler (1984)
Urea	Water	0.136	0.138	Cussler (1984)
Benzene	Chloroform	2.11	2.10	Grushka and Kikta (1974)
			2.30	Timmermans (1959)
Toluene	Chloroform	2.00	2.01	Grushka and Kikta (1974)
Methyl red	Tetrahydrofuran	1.22	1.60	Landry et al. (1988)
50K PS	Tetrahydrofuran	0.071	0.075	Wesson et al. (1985)—46K PS
Benzene	Cyclohexane	1.66		
Toluene	Cyclohexane	1.60		
Anthracene	Cyclohexane	1.14		
9-methyl anthracene	Cyclohexane	1.04		
Benzil	Cyclohexane	0.993		
10K PS-A	Cyclohexane	0.137	0.125	Barooah and Chen (1985)—9K PS
17K PS-A	Cyclohexane	0.093		
50K PS-A	Cyclohexane	0.043		
88K PS-A	Cyclohexane	0.039		

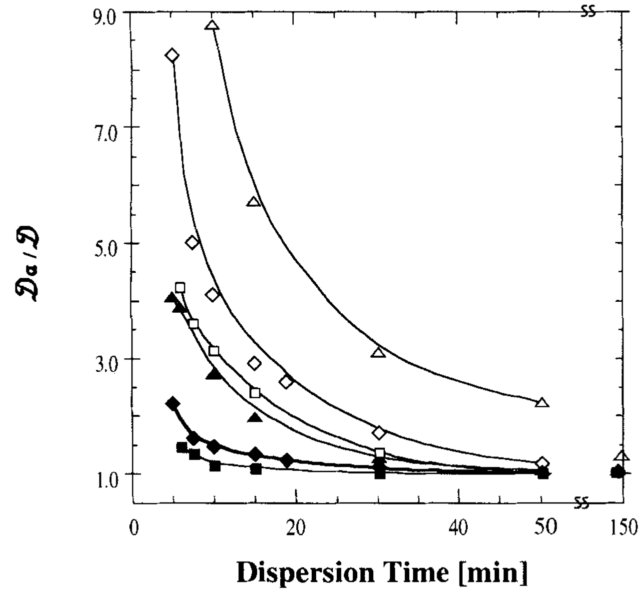


Figure 2. Ratio of the apparent to true diffusion coefficient $\mathfrak{D}_a/\mathfrak{D}$, as a function of dispersion time at 25°C.

Coiled tube measurements: 10K PS-A (△) and anthracene (◇) in THF, and anthracene in 100 g/l PS/THF (□). "Square-shaped" tube measurements: 10K PS-A (▲) and anthracene (◆) in THF, and anthracene in 100 g/L PS/THF (■). Curves are drawn to guide the eye, and do not have any other physical significance.

profiles are fit well by Eq. 5 with $r^2 > 0.999$. At 400 g/L PS, $\mathfrak{D}$ is reduced 82% from its value in pure THF (1.58×10^{-5} cm^2/s). This demonstrates the sensitivity of Taylor dispersion to the range of diffusivities associated with probe diffusion in polymer solutions.

To investigate the effect of tube curvature on measurements of apparent diffusivity $\mathfrak{D}_a$, measurements were made as a function of dispersion time or fluid velocity for three systems using the coiled tube and the "square-shaped" tube. Figure 2 shows that $\mathfrak{D}_a$ plateaus to the true diffusivity at long dispersion times in accordance with the theory by Janssen (1976). As expected, in all cases, deviations from the true diffusivity were higher in the coiled tubing than in the "square-shaped" tube, meaning that measurements taken with coiled tubing require longer dispersion times in order to obtain true diffusivities. In the case of 10K PS-A ($\mathfrak{D} \sim 10^{-6}$ cm^2/s) the true value of $\mathfrak{D}$ could not be measured using the coiled tube at the lowest pump setting; $\mathfrak{D}_a$ for the coiled tube at a dispersion time of 150 min. was about 10% higher than that measured with the "square-shaped" tube. The problem is alleviated as $\mathfrak{D}$ is increased (Sc is decreased) as $\mathfrak{D}_a/\mathfrak{D}$ for anthracene is less than that for 10K PS-A. Also, increasing the viscosity alleviates the problem (*Re* decreases) as $\mathfrak{D}_a/\mathfrak{D}$ for anthracene in 100 g/L PS in THF is lower than in neat THF. It should be noted that curvature effects are more important in THF systems than in higher viscosity solvent systems, such as water, used in the work of Pratt and Wakcham (1975). For studies in polymer solutions, where both $\mathfrak{D}$ and viscosity change with polymer concentration, curvature effects were avoided by use of the "square-shaped" tube.

To investigate the effects of solute (probe) molecular weight and molar volume, $\mathfrak{D}$ was measured at 25 and 50°C for 18 different solutes in THF. The data, summarized in Table 2, are useful in several ways. For example, information regarding diffusion of methyl methacrylate, styrene, and benzoyl peroxide may be used in the interpretation of free-radical polymerization studies (Achilias and Kiparissides, 1992). Diffusion coefficients of solvents such as benzene, toluene, and chloroform may be of value in this same context (Wisnudel and Torkelson, 1994). Other molecules listed in Table 2 are chromophores commonly used in fluorescence and phosphorescence studies, and their diffusion data may be useful in interpreting diffusion-controlled luminescence interactions. For example, $\mathfrak{D}$ for anthracene is 12% greater than for ben-

Table 2. Diffusion Coefficients of Probe Molecules in Tetrahydrofuran

Probe Molecule (No Polystyrene Present)	MW g/mol	Molar Vol. cm^3/mol	$\mathfrak{D}\times10^5$ 25°C cm^2/s	Wilke-Chang % Error	$\mathfrak{D}\times10^5$ 50°C cm^2/s	Wilke-Chang % Error
Benzene	78	97	2.59	1.5	3.31	3.9
Biacetyl	86	111	2.52	−4.4	3.15	0.5
Toluene	92	119	2.33	−0.7	3.05	−0.6
Aniline	93	102	2.03	25.1	2.50	33.1
Methyl Methacrylate	100	126	2.15	4.0	2.82	4.4
Styrene	104	133	2.01	7.8	2.52	12.6
2,3-hexanedione	114	163	1.90	0.8	2.67	−5.6
Chloroform	119	92	2.20	22.7	2.73	29.5
Naphthalene	128	157	1.80	8.9	2.33	10.1
Anthracene	178	214	1.58	3.3	1.92	11.3
Pyrene	202	228	1.45	7.9	1.90	7.8
Benzil	210	229	1.39	12.6	1.68	21.9
Benzoyl peroxide	242	258	1.24	17.2	1.69	12.9
Methyl red	269	315	1.22	5.9	1.53	10.1
9,10-diphenylanthracene	330	391	1.05	7.9	1.39	7.4
9,10-bis(phenyl ethynyl)anthracene	378	450	0.91	14.2	1.23	11.4
Decacyclene	451	523	1.00	4.5	1.32	4.5
Rubrene	533	605	0.77	13.0	1.03	11.1

% Error = 100 × (calc. − exp.)/exp.

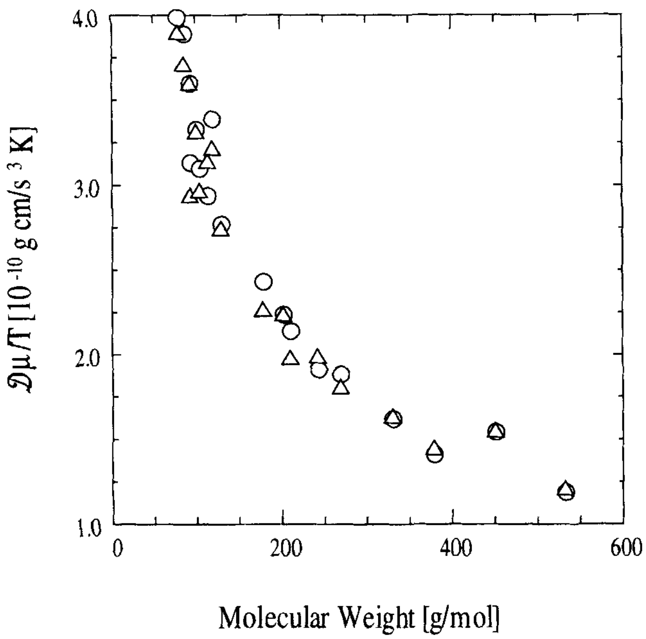


Figure 3. Diffusion coefficient of probe molecules in THF at 25°C (○) and 50°C (△) rescaled by viscosity and temperature as a function of molecular weight.

zil, in qualitative agreement with phosphorescence quenching studies by Gebert et al. (1992). Figure 3 shows the solute molecular weight dependence of $\mathfrak{D}$ scaled by viscosity and temperature. $\mathfrak{D}\mu/T$ is essentially constant for each solute/solvent system. Using data from all of the solutes at 25 and 50°C, an average apparent activation energy of 2.0 ± 0.3 kcal/mol was obtained, with no apparent correlation of activation energy with solute size.

In Figure 4, values of $\mathfrak{D}$ from Table 2 are compared to those predicted by the Wilke-Chang correlation and Stokes-Einstein equation. The Wilke-Chang correlation is (Wilke and Chang, 1955)

$$\mathfrak{D} = 7.4 \times 10^{-8} \frac{T(M_s\phi)^{0.5}}{\mu V^{0.6}} \tag{6}$$

where M_s is the molecular weight of the solvent (g/mol), ϕ is an association factor for the solvent which is taken to be 1.0 for THF, and V is the molar volume of the solute at its normal boiling point (cm^3/mol). Values of V were calculated from the atomic contribution method of Le Bas (Reid et al., 1987). A fit of Eq. 6 to the data yielded a correlation coefficient of $r^2 = 0.86$ at 25°C, and a $r^2 = 0.79$ for the data at 50°C. Linear regression of the data revealed that r^2 could be improved to 0.93 at 25°C and 0.89 at 50°C by using a slope of 6.8×10^{-8}. This represents an average error of 8%, within the claims of Wilke and Chang. The Stokes-Einstein equation $\mathfrak{D} = k_B T/(6\pi\mu r)$ where k_B is Boltzmann's constant has a smaller dependence on V than Eq. 6. Here, the solute radius r is calculated from $(3V/4\pi)^{1/3}$, although other methods for estimating r may be equally appropriate (Edward, 1970). Thus, as V is decreased to the size of a THF molecule, the deviation from the Stokes-Einstein equation increases. This is expected since the Stokes-Einstein equation is derived based on the diffusion of a rigid solute sphere in a continuum of solvent. It has been found that the Stokes-Einstein equation fails when the solute size (radius) is less than five times that of the solvent (Chen et al., 1981). This supports the observation that values of Stokes radii calculated from $\mathfrak{D}$ and the Stokes-Einstein equation can differ from the actual van der Waals radius of the molecule (Ghai et al., 1973). Significant effort, both from a theoretical and empirical standpoint, has been placed on improving upon the predictive capability of the Stokes-Einstein equation. A number of empirical correlations, including Eq. 6, have been compiled by Reid et al. (1987). From a theoretical viewpoint, both the microfriction theory of Gierer and Wirtz (1953) as recently applied by Chen and coworkers (1984, 1985) and an application of Kirkwood-Riseman theory by Espinosa and Garcia de la Torre (1987) have been successful in interpreting tracer diffusion in binary systems. These theories introduce a friction factor f into the denominator of the Stokes-Einstein equation, thus reducing the Stokes drag to account for the failure of continuum hydrodynamics at molecular dimensions. Additionally, rough-hardsphere theories have been successful in modeling the tracer diffusion of spherically-shaped solutes (Chen et al., 1981, 1983, 1985; Pollack et al., 1990).

To investigate the dependence of ternary probe diffusion on polymer solution concentration, anthracene, benzil, and methyl red diffusion were measured in solutions containing up to 400 g/L PS at 25°C. These data are summarized in Table 3. Figure 5 shows the decrease with polymer concentration of the natural logarithm of the probe diffusion coefficient, $\mathfrak{D}_p$, normalized to its value at zero polymer concentration, $\mathfrak{D}_{p0}$. These data are in agreement with $\mathfrak{D}_p/\mathfrak{D}_{p0}$ for methyl red by Landry et al. (1988), though the value of $\mathfrak{D}_{p0}$

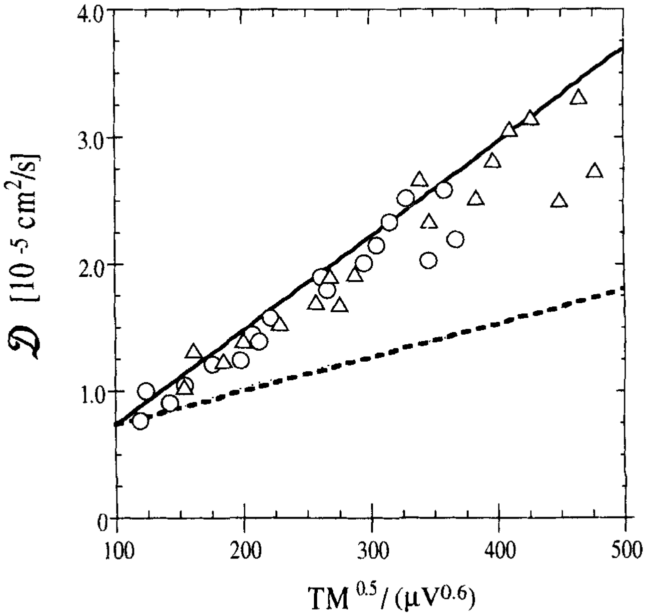


Figure 4. Diffusion coefficient of probe molecules in THF at 25°C (○) and 50°C (△) as a function of TM$^{0.5}$/($\mu V^{0.6}$) from the Wilke-Chang correlation.

The Stokes-Einstein equation (– – –) is also plotted for comparison.

Table 3. Effect of Polymer Concentration on Probe Diffusion Coefficients in Polystyrene-Tetrahydrofuran Solutions

Polymer Conc. g/L	$\mathfrak{D}_p/\mathfrak{D}_{po}$ at 25°C		
	Anthracene	Benzil	Methyl Red
100	0.79	0.75	0.72
200	0.54	0.50	0.46
300	0.41	0.33	0.32
400	0.18	0.16	0.13

varies slightly from theirs. The solid curve represents the normalized solvent (THF) self-diffusion coefficient, $\ln(\mathfrak{D}_s/\mathfrak{D}_{s0})$, as predicted by the free volume theory of Vrentas and Duda (1977, 1982, 1984). The theory, as extended to ternary systems by Ferguson and von Meerwall (1980), predicts that $\ln(\mathfrak{D}_p/\mathfrak{D}_{po}) = \xi_{p,s} \ln(\mathfrak{D}_s/\mathfrak{D}_{so})$ where $\xi_{p,s}$ is the ratio of the "jumping-unit size" of the probe to that of the solvent, provided that the concentration of probe is negligible. By regression analysis, $\xi_{p,s} = 1.0_9$ for anthracene, 1.1_6 for benzil, and 1.2_6 for methyl red. The values of $\xi_{p,s}$ for anthracene and benzil support the polymer concentration dependence of phosphorescence quenching rate data by Gebert et al. (1992). The apparent correlation of $\xi_{p,s}$ with the size of these probes is interesting and warrants further investigation of $\xi_{p,s}$ for other probes in Table 2.

This study, which is the first to measure $\mathfrak{D}$ of ternary probes in polymer solutions using Taylor dispersion, has shown this method to be attractive in terms of its simplicity and applicability to a wide assortment of experimental conditions. By using variable-wavelength UV absorbance and differential refractometer detectors and constructing an apparatus that minimizes tube curvature effects, measurements can be made in multicomponent polymer solutions, such as those reported here, resulting in the smallest values of $\mathfrak{D}$ measured by Taylor dispersion. While the range of diffusivities measurable by other established techniques such as NMR ($>10^{-10}$ cm²/s), dynamic light scattering ($>10^{-12}$ cm²/s), forced Rayleigh scattering or fluorescence photobleaching ($>10^{-14}$ cm²/s) is greater than that obtainable by Taylor dispersion, diffusivities of most small molecules in semidilute and reasonably concentrated polymer solutions fall within the range accessible by Taylor dispersion (10^{-5}–10^{-7} cm²/s). This range is also sufficient for measurements of D for polymers of molecular weight as high as 100–150 kg/mol in dilute solution. Taylor dispersion measurements are inexpensive, fast, require small quantities (ng) of solute, need no calibration, and can be automated with HPLC technology available in many chemical laboratories. Also, the ability to use a multitude of detector methods allows for measurement of a wide assortment of solutes and solvents, making this technique well-suited for investigations into the effects of molecular size and shape on probe diffusion. Other techniques are limited by the number of probes that can be used; for example, forced Rayleigh scattering is limited to photoisomerizable molecules. Given these advantages and the fact that calculation of $\mathfrak{D}$ from dispersion data is straightforward, it is likely that Taylor dispersion will see greater application, especially in diffusion studies involving polymer solutions.

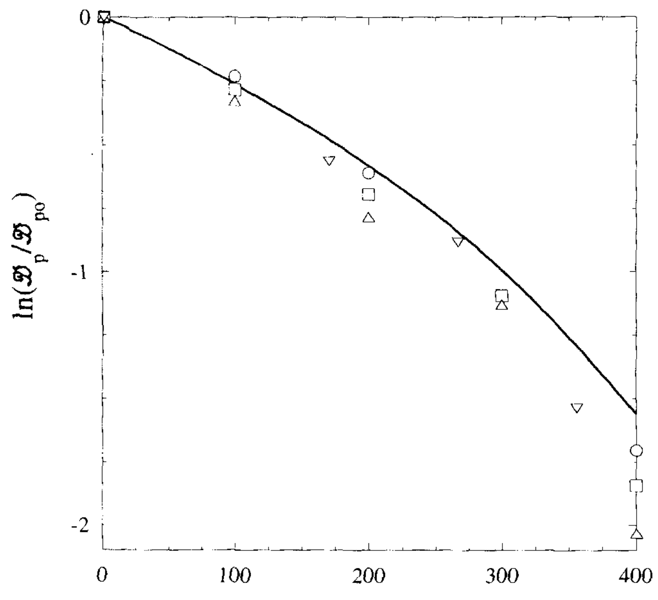


Figure 5. Natural logarithm of probe diffusion coefficient divided by its value at zero polymer concentration as a function of polystyrene concentration in THF at 25°C for anthracene (○), benzil (□), and methyl red (△).

Also plotted are the data for methyl red (▽) from Landry et al. (1988), and the free-volume prediction of $\ln(\mathfrak{D}_s/\mathfrak{D}_{so})$ for the solvent-self-diffusion of THF (——).

Acknowledgments

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Notation

A = detector fitting parameter
B = detector fitting parameter
C = mean concentration of solute, g/cm³
$\mathfrak{D}_a$ = apparent diffusion coefficient, cm²/s
Dn = Dean number ($\lambda^{-0.5}Re$)
$\mathfrak{D}_p$ = probe diffusion coefficient, cm²/s
$\mathfrak{D}_{p0}$ = probe diffusion coefficient at zero polymer concentration, cm²/s
$\mathfrak{D}_s$ = solvent self diffusion coefficient, cm²/s
$\mathfrak{D}_{s0}$ = solvent self diffusion coefficient at zero polymer concentration, cm²/s
M = polymer molecular weight, g/mol
$\bar{M}_n$ = polymer number average molecular weight, g/mol
$\bar{M}_w$ = polymer weight average molecular weight, g/mol
r = solute radius, cm
R_c = coil radius, cm
Re = Reynolds number ($2\bar{U}a\rho/\mu$)
Sc = Schmidt number ($\mu/\rho\mathfrak{D}$)
T = absolute temperature, K

Greek letters

λ = ratio of the coil radius to tube radius (R_c/a)
μ = viscosity, g/cm·s
$\xi_{p,s}$ = ratio of probe and solvent jumping units
σ^2 = variance, min

Literature Cited

Achilias, D. S., and C. Kiparissides, "Development of a General Mathematical Framework for Modeling Diffusion-Controlled Free-Radical Polymerization Reactions," *Macromol.*, **25**, 3739 (1992).

Al-Naafa, M. A., and M. S. Selim, "Measurement of Diffusion Coefficients by Taylor's Method of Hydrodynamic Stability," *AIChE J.*, **40**, 1412 (1994).

Alizadeh, A., C. A. Nieto de Castro, and W. A. Wakeham, "The Theory of the Taylor-Dispersion Technique for Liquid Diffusivity Measurements," *Int. J. Thermophys.*, **1**, 243 (1980).

Aris, R., "On the Dispersion of a Solute in a Fluid Flowing Through a Tube," *Proc. R. Soc. Lond. Ser. A*, **235**, 67 (1956).

Barooah, A., and S. H. Chen, "Translational Diffusion of Polystyrene in Cyclohexane at Infinite Dilution from 283 to 348 K," *J. Poly. Sci.: Poly. Phys. Ed.*, **23**, 2457 (1985).

Barooah, A., C. K. J. Sun, and S. H. Chen, "Translational Diffusion of Polystyrene in 1,4-Dioxane at Infinite Dilution Determined with the Extended Taylor Dispersion Method," *J. Poly. Sci.: Poly. Phys. Ed.*, **24**, 817 (1986).

Bello, M. S., R. Rezzonico, and P. G. Righetti, "Use of Taylor-Aris Dispersion for Measurement of a Solute Diffusion Coefficient in Thin Capillaries," *Science*, **266**, 773 (1994).

Boggs, D. R., "Diffusive Transport in Membranes for Immunoisolation," PhD Thesis, Northwestern Univ. (1994).

Burkey, T. J., D. Griller, D. A. Lindsay, and J. C. Scaiano, "Simple Method for Quantifying the Distribution of Organic Substrates between the Micellar and Aqueous Phases of Sodium Dodecyl Sulfate Solution," *J. Amer. Chem. Soc.*, **106**, 1983 (1984).

Chen, H. C., and S. H. Chen, "Diffusion of Crown Ethers in Alcohols," *J. Phys. Chem.*, **88**, 5118 (1984).

Chen, H. C., and S. H. Chen, "Taylor Dispersion Measurement of the Diffusivities of Polymethylenes in Dilute Solutions," *Chem. Eng. Sci.*, **40**, 521 (1985).

Chen, S. H., H. T. Davis, and D. F. Evans, "Tracer Diffusion in Polyatomic Liquids: II," *J. Chem. Phys.*, **75**, 1422 (1981).

Cussler, E. L., *Diffusion*, Cambridge Univ. Press, New York (1984).

Duda, J. L., J. S. Vrentas, S. T. Ju, and H. T. Liu, "Prediction of Diffusion Coefficients for Polymer-Solvent Systems," *AIChE J.*, **28**, 279 (1982).

Edward, J. T., "Molecular Volumes and the Stokes-Einstein Equation," *J. Chem. Ed.*, **47**, 261 (1970).

Espinosa, P. J., and J. Garcia de la Torre, "Theoretical Prediction of Translational Diffusion Coefficients of Small Rigid Molecules from Their Molecular Geometry," *J. Phys. Chem.*, **91**, 3612 (1987).

Ferguson, R. D., and E. von Meerwall, "Free Volume Interpretation of Self-Diffusion in Ternary Systems," *J. Poly. Sci., Poly. Phys. Ed.*, **18**, 1285 (1980).

Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca (1953).

Gebert, M. S., D. H.-S. Yu, and J. M. Torkelson, "Diffusion-Limited Polymer-Small Molecule Interactions: A Study of Phosphorescence Quenching," *Macromol.*, **25**, 4160 (1992).

Ghai, R. K., H. Ertl, and F. A. L. Dullien, "Liquid Diffusion of Nonelectrolytes: 1," *AIChE J.*, **19**, 881 (1973).

Ghai, R. K., H. Ertl, and F. A. L. Dullien, "Liquid Diffusion of Nonelectrolytes: 2," *AIChE J.*, **20**, 1 (1974).

Grushka, E., and E. J. Kikta, "Extension of the Chromatographic Broadening Method of Measuring Diffusion Coefficients to Liquid Systems. I. Diffusion Coefficients of Some Alkylbenzenes in Chloroform," *J. Phys. Chem.*, **78**, 2297 (1974).

Hammond, B. R., and R. H. Stokes, "Diffusion in Binary Liquid Mixtures," *Trans. Farad. Soc.*, **49**, 890 (1953).

Huggenberger, C., J. Lipscher, and H. Fischer, "Self-Termination of Benzoyl Radicals to Ground- and Excited-State Benzil. Symmetry Control of a Radical Combination," *J. Phys. Chem.*, **84**, 3467 (1980).

Janssen, L. A. M., "Axial Dispersion in Laminar Flow through Coiled Tubes," *Chem. Eng. Sci.*, **31**, 215 (1976).

Landry, M. R., Q. Gu, and H. Yu, "Probe Molecule Diffusion in Polymer Solutions," *Macromol.*, **21**, 1158 (1988).

Leaist, D. G., "Determination of Ternary Diffusion Coefficients by the Taylor Dispersion Method," *J. Phys. Chem.*, **94**, 5180 (1990).

Levenspiel, O., and W. K. Smith, "Notes on the Diffusion-Type Model for the Longitudinal Mixing of Fluids in Flow," *Chem. Eng. Sci.*, **6**, 227 (1957).

Metaxiotou, Z. A., and S. G. Nychas, "Experimental Measurement of Diffusion in Aqueous Polyvinylpyrrolidone Solutions," *AIChE J.*, **41**, 812 (1995).

Ouano, A. C., "Diffusion in Liquid Systems: I. A Simple and Fast Method of Measuring Diffusion Constants," *Ind. Eng. Chem. Fundam.*, **11**, 268 (1972).

Pollack, G. L., R. P. Kennan, J. F. Himm, and D. R. Stump, "Diffusion of Xenon in Liquid Alkanes: Temperature Dependence Measurements with a New Method. Stokes-Einstein and Hard Sphere Theories," *J. Chem. Phys.*, **92**, 625 (1990).

Pratt, K. C., and W. A. Wakeham, "The Mutual Diffusion Coefficient of Ethanol-Water Mixtures: Determination by a Rapid, New Method," *Proc. R. Soc. Lond. A*, **336**, 393 (1974).

Pratt, K. C., and W. A. Wakeham, "The Mutual Diffusion Coefficient for Binary Mixtures of Water and the Isomers of Propanol," *Proc. R. Soc. Lond. A.*, **342**, 401 (1975).

Price, W. E., "Theory of the Taylor Dispersion Technique for Three-Component-System Diffusion Measurements," *J. Chem. Soc. Farad. Trans.* 1, **84**, 2431 (1988).

Reid, R. C., J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed., McGraw-Hill, New York (1987).

Sun, C. K. J., Y. F. Maa, and S. H. Chen, "Translational Diffusion of Relatively Short Polystyrene Chains in Cyclohexane: II. An Interpretation of Hydrodynamic Radius with the Freely Jointed Chain Model," *J. Poly. Sci.: Poly. Phys. Ed.*, **25**, 1473 (1987).

Taylor, G., "Dispersion of Soluble Matter in Solvent Flowing Slowly through a Tube," *Proc. R. Soc. Lond. Ser. A*, **219**, 186 (1953).

Taylor, G., "Conditions Under Which Dispersion of a Solute in a Stream of Solvent can be Used to Measure Molecular Diffusion," *Proc. R. Soc. Lond. Ser. A.*, **225**, 473 (1954).

Timmermans, J., *Physico-Chemical Constants of Binary Systems*, Vol. 1, Interscience, New York (1959).

Tyrrell, H. J. V., and K. R. Harris, *Diffusion in Liquids*, Butterworths, London (1984).

Vrentas, J. S., and J. L. Duda, "Diffusion in Polymer-Solvent Systems: I. Re-examination of the Free-Volume Theory," *J. Poly. Sci., Poly. Phys. Ed.*, **15**, 403 (1977).

Vrentas, J. S., J. L. Duda, and H.-C. J. Ling, "Self-Diffusion in Polymer-Solvent-Solvent Systems," *J. Poly. Sci., Poly. Phys. Ed.*, **22**, 459 (1984).

Wilke, C. R., and P. Chang, "Correlation of Diffusion Coefficients in Dilute Solutions," *AIChE J.*, **1**, 264 (1955).

Wisnudel, M. B., and J. M. Torkelson, "Diffusion-limited Photophysical Interactions as in Situ Probes of Conversion in Free Radical Polymerization: Quantitative Analysis with Predictive Free-Volume Theory," *Macromol.*, **27**, 7217 (1994).

Yumet, E., H. C. Chen, and S. H. Chen, "Tracer Diffusion of Carbon Tetrachloride, S-Trioxane, 12-Crown-4, 15-Crown-5, 18-Crown-6 in Acetonitrile, Benzene, and Chlorobenzene," *AIChE J.*, **31**, 76 (1985).

Yu, D. H.-S., and J. M. Torkelson, "Diffusion-Limited Phosphorescence Quenching Interactions in Polymer Solutions: Small Molecule-Small Molecule Interactions Interpreted by Free Volume Theory," *Macromolecules*, **21**, 1033 (1988).

Zielinski, J. M., and J. L. Duda, "Predicting Polymer/Solvent Diffusion Coefficients Using Free Volume Theory," *AIChE J.*, **38**, 405 (1992).

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