

Universal Calibration for Thermal Field-Flow Fractionation

GAO YUSHU* and CHEN XIURONG

Institute of Chemistry, Academia Sinica, Beijing, People's Republic of China

SYNOPSIS

Experiments have shown that the thermal diffusion coefficient of a polymer is independent of the sample's molecular weight. According to the relationship between the ordinary diffusion coefficient and polymer molecular weight, a universal calibration method for thermal field-flow fractionation (FFF) has been created. This method has been examined experimentally by three polymers of different chemical composition with different molecular weight in three organic solvents. It is shown that this method is useful both in terms of calibrating a thermal FFF system with some readily available polymer standard, for use with unknown samples of known thermal diffusivity, and in terms of determining the thermal diffusion coefficient of the unknown sample under conditions where its molecular weight can be measured by other methods.

INTRODUCTION

A relatively new family of separation methods called field-flow fractionation (FFF) permits the characterization of a wide variety of particles and soluble macromolecules in the broad MW range of 10^3 – 10^{16} g/mol, corresponding to particle diameters in the 10^{-3} to 10^2 μm range.^{1,2} FFF, sometimes described as one-phase chromatography, is performed in a thin open channel. There is no separate stationary phase used in this channel; instead, retention results from the redistribution of solute from fast- to slow-moving streams of the laminar flow profile generated within the flowing liquid mobile phase.

Most frequently, the high-resolution thermal FFF (TFFF) method³ is used to separate nonaqueous solutions of relatively nonpolar polymers. Here, a temperature gradient is established between parallel, highly polished copper bars, sandwiched around an insulating spacer in which the flow channel is cut. Solutes are transported by thermal diffusion toward the cold wall (accumulation wall). This transport is opposite by diffusion, and at equilibrium the two fluxes are exactly in balance. At this point, the solute is found in an exponential cloud whose mean concentration is at the interface between the channel

fluid and the cold wall. As in all FFF methods, separation results from different solutes being forced to different average distances from the wall, where they are intercepted by different flow-stream velocities. In TFFF, each molecular species assumes a unique characteristic layer thickness within the channel whose magnitude depends, on the one hand, on such sample properties as the thermal and ordinary diffusivity, and on the other on the operational parameters field strength and channel geometry. The component concentration at distance x from the accumulation wall is:

$$c(x) = c_0 \exp(-x/l), \quad (1)$$

where c_0 is the concentration at the wall interface and l is the characteristic thickness, approximately equal to the distance from the wall to the center of gravity of the exponential profile. Since the concentration layers of smaller molecules or particles extend further toward the center of the channel, where flow velocity is larger, these small particles move faster on the average than larger particles that are confined to slower flow-streams nearer the wall.

Of great importance to the mathematical linkage of theory and experiment is the retention parameter λ , which is a dimensionless form of l :

$$\lambda = l/w, \quad (2)$$

* To whom correspondence should be addressed.

where w is the channel thickness. The retention ratio, R , is defined as the ratio of the channel void volume V_0 to the retention volume V_r of the eluted species. In turn, R is found to be related to λ by

$$R = 6\lambda[\coth(1/2 \lambda) - 2\lambda] \quad (3)$$

or, for highly retained samples,

$$R = 6\lambda. \quad (3a)$$

In the case of TFFF, λ may be expressed as¹:

$$\lambda = D/D_T\Delta T, \quad (4)$$

where D is the polymer-solvent diffusion coefficient, D_T is the thermal diffusion coefficient, and ΔT is the temperature difference across the channel. As an elution technique, TFFF can be used for determination of polymer molecular weight and molecular weight distribution. Although, in principle, the dependence of retention on sample MW can be calculated theoretically, this is often difficult to do since thermal diffusivities are largely unknown; as in size exclusion chromatography, a calibration curve is, therefore, usually needed for a particular system under fixed experimental conditions. Experiments have shown that the relevant retention is dependent not only on molecular weight but also on polymer composition.^{4,5} Therefore, the method cannot conveniently be used for molecular weight determination of unknown samples without access to standards of narrow molecular weight distribution of the polymer in question to calibrate the system. For size exclusion chromatography, this problem has been solved by Benoit et al.,⁶ who used the hydrodynamic volume as the separation parameter (so-called universal calibration). For different types of samples, a plot of $\log [\eta]M$ vs. elution volume V_e gives a single linear relationship in the range of effective separation of the SEC column. In this work, we are investigating the possibility of finding a universal calibration for the TFFF system.

In the case of TFFF, the retention is expressed in terms of two physical-chemical parameters: the ordinary (Fick's) diffusion coefficient, D , and the thermal diffusion coefficient, D_T , as shown in eq. (4). Experiments have shown that D_T depends solely on solvent and polymer composition but is independent on a sample's molecular weight.^{7,8} The ordinary diffusion coefficient at infinite dilution is given by the Stokes-Einstein equation, which can be related to the intrinsic viscosity, $[\eta]$, by the expression⁹

$$D = \frac{R'T}{6\pi\eta N} \left[\frac{10\pi N}{3M[\eta]} \right]^{1/3} \quad (5)$$

or

$$D = \frac{R'T}{6\pi\eta N} \left[\frac{10\pi N}{3kM^{\alpha+1}} \right]^{1/3} \quad (6)$$

where η is the solvent viscosity, R' is the gas constant, T is the temperature, N is Avogadro's number, and α and k are Mark-Houwink coefficients for the solvent-solute pair.

A combination of eqs. (3a), (4), and (6) gives the following relationship between a sample's retention ratio, R , and its molecular weight, M , and thermal diffusion coefficient, D_T :

$$R = AD_T^{-1} (kM^{\alpha+1})^{-1/3}, \quad (7)$$

where

$$A = R'T(\pi\eta N\Delta T)^{-1} (10\pi N/3)^{1/3} \quad (8)$$

is a constant under the same experimental condition. Equation (7) can be used as a universal calibration procedure if values of D_T , k , and α are available from independent experiments or from the literature.

EXPERIMENTAL

Figure 1 shows the schematic diagram of a TFFF apparatus. The channel, sandwiched between two chrome-plated bars, is 45.8 cm in tip-to-tip length, 2.0 cm in breadth, and 0.0254 cm in thickness. A controllable temperature gradient can be applied across the channel by means of electrical cartridge heaters inserted into the upper bar, and heat is removed from the lower bar by circulating tap water. The hot-wall temperature is controlled by a transformer and a voltage stabilizer. As the cold-wall temperature is influenced by the flow rate of tap water, which is unstable in our laboratory, we built a special apparatus to control this flow rate. A schematic of the apparatus is shown in Figure 2, where 1 is the thermocouple thermometer and 2 and 3 are electromagnetic switches. If the cold-wall temperature exceeds a predetermined setpoint temperature, a signal is sent to the "high" controller, which activates switch 3 to increase flow of tap water. Conversely, if the temperature is too low, a signal is sent from the "low" controller, activating switch 2, which diverts tap water from the system through the by-

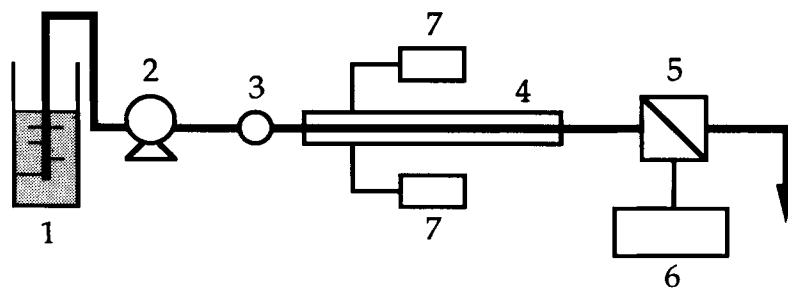


Figure 1 Schematic diagram of TFFF apparatus. (1), reservoir; (2), pump; (3), sample injector; (4), TFFF channel; (5) RI detector (Waters 401); (6), recorder; (7), T_H -control; (8), T_c -control. $L = 45.8$ cm, $b = 2.0$ cm, $w = 0.0254$ cm, $T_H = 62^\circ\text{C}$, $T_c = 22^\circ\text{C}$, flow rate = 0.23 mL/min.

pass channel. In this way, T_c was easily controlled in the range of $\pm 0.2^\circ\text{C}$, resulting in a stable base line. In this work, the cold temperature was kept at 22°C while the ΔT was maintained at 40°C . The carrier solvents were delivered by a Milton Roy pump with a flow rate of 0.23 mL/min. The concentration of eluting polymer was detected by an RI detector (Waters, R-401). A strip-chart recorder was used to monitor the detector response.

The polymer standards used in this study are described in Table I. The lowest molecular weight is 35,000 and the highest is 900,000.

Three organic solvents [tetrahydrofuran (THF), methyl(ethyl ketone) (MEK), and toluene] were used as carriers. Table II shows parameters for these

polymer-solvent pairs. These parameters were found from the literature and from handbooks.^{10,11}

RESULTS AND DISCUSSION

The range of commercially available narrow standards are limited to polystyrene (PS), poly(methyl methacrylate) (PMMA), and a small number of others. For the purpose of developing a good calibration curve, we chose to work with PS, PMMA, and poly(αmethylstyrene) (PαMS). The experimentally measured retention ratio, R , for these standard polymers in different solvents are listed in Tables III and IV. T_{cg} is the temperature formed a

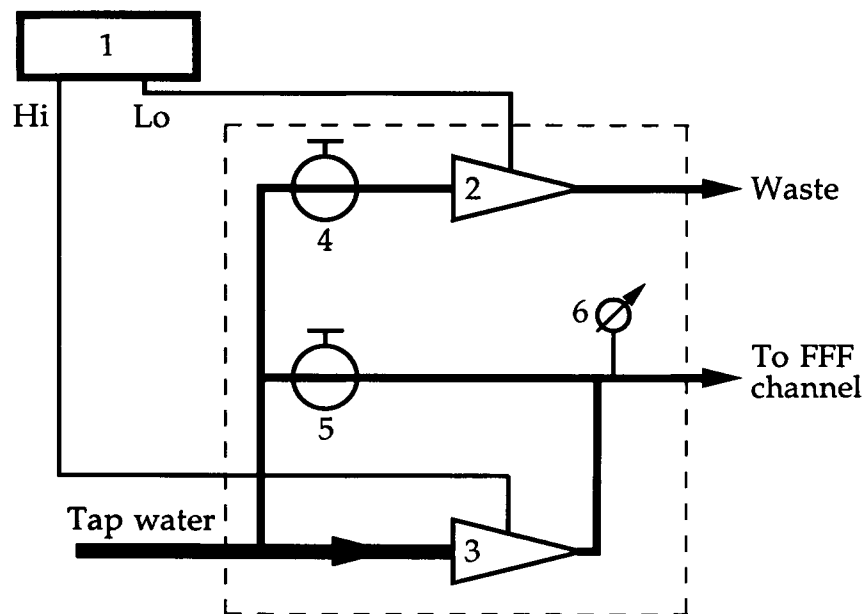


Figure 2 Cold-wall temperature, T_c , control. (1), thermocouple thermometer (Cole-Parmer); (2, 3), electromagnetic switch; (4, 5), mitering valve (Nupro); (6), gauge.

Table I Description of Polymers Used in This Study

Sample	MW (10^{-3})	MWD (M_w/M_n)	Source
PS	35	1.06	Pressure Chemical
	110	1.1	Pressure Chemical
	200	1.1	Pressure Chemical
	498	1.2	Pressure Chemical
	670	1.15	Pressure Chemical
900	Not given	du Pont	
PMMA	107	1.1	Pressure Chemical
	240	1.09	Pressure Chemical
	330	1.1	Pressure Chemical
	400	1.14	Pressure Chemical
PaMS	139	1.05	Polymers Lab.
	380	1.05	Polymers Lab.

distance l from the cold wall [eq. (1)] assuming a linear temperature gradient $dT/dx = \Delta T/w$. T_{cg} may be calculated as

$$T_{cg} = T_c + \Delta T \lambda. \quad (9)$$

At a ΔT of 42°C , the difference between values of T_{cg} corresponding to PS 35,000 and 900,000 is about 4°C in THF.

Figures 3 to 5 show the plots of the retention ratio, R , vs. $D_T^{-1}(kM^{\alpha+1})^{-1/3}$ for PS, PMMA, and PaMS in different solvents. The experimental points are arranged around single lines independently of composition of polymer. Given the relationship between molecular weight and retention in TFFF, this calibration procedure is therefore universal. By contrast, the two curves shown in Figure 6 represent "regular" FFF calibration curves for two sets of polymer standards, namely, PS and PMMA, analyzed in THF. The lack of overlap between the two is a clear indication of differences in their D_T ,

Table II Polymer-Solvent Parameters

Polymer-Solvent	$D_T \times 10^7$	$k \times 10^5$ ^a	α ^a
PS-THF	0.92	1.41	0.79
PS-Toluene	1.00	17.0	0.69
PS-MEK	1.41	39.0	0.58
PMMA-THF	1.28	1.04	0.697
PMMA-Toluene	1.63	7.1	0.73
PMMA-MEK	1.5	6.8	0.72
PaMS-Toluene	1.19	7.81	0.73

^a k and α were measured at 25°C .

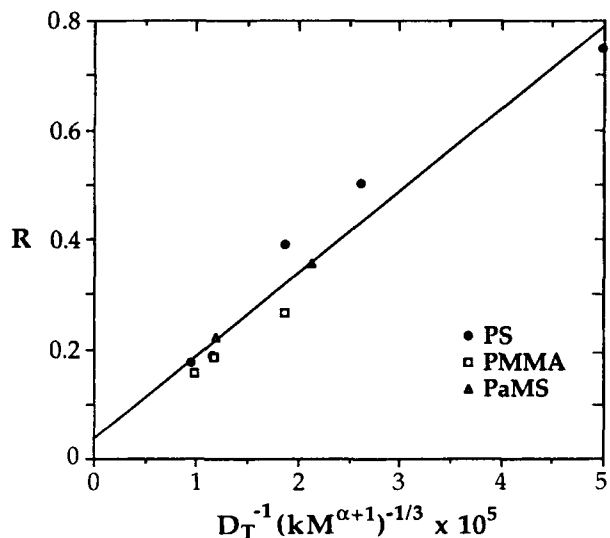


Figure 3 Retention ratio, R , vs. $D_T^{-1}(kM^{\alpha+1})^{-1/3}$ for different polymer samples with different molecular weights. Carrier was toluene. Values for D_T , k , and α are obtained from references 10 and 11.

α , and k values. This, in turn, highlights the need to use the universal calibration procedure proposed here, which effectively combined the same two data sets into the single curve in Figure 5.

In the previous discussion, we ignored the thermal expansion of the solvent and the distortion of the velocity profile due to temperature effect on the carrier viscosity. Experiments have shown that such distortion does not have a profound effect on reten-

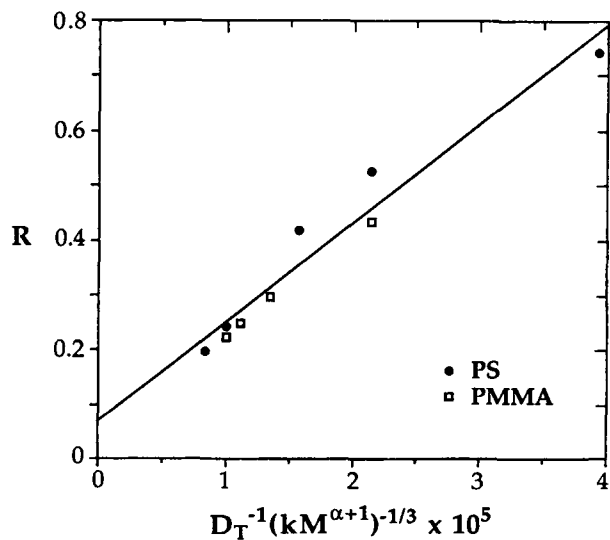


Figure 4 Retention ratio, R , vs. $D_T^{-1}(kM^{\alpha+1})^{-1/3}$ for different polymer samples with different molecular weights. Carrier was MEK.

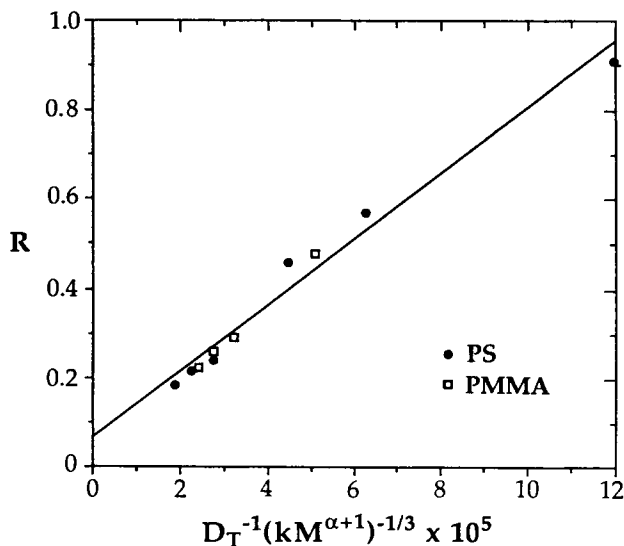


Figure 5 Retention ratio, R , vs. $D_T^{-1}(kM^{\alpha+1})^{-1/3}$ for different polymer samples with different molecular weights. Carrier was THF.

tion under experimental conditions involving ΔT values less than 50°C . We must now examine the influence of temperature on D and D_T , as both of these quantities will vary with T_{cg} . There is very limited information about the relationship between D , D_T , and temperature. The following expressions for D and D_T as functions of temperature describe the behavior of PS in ethylbenzene^{7,12}:

$$D = M^{-0.552} \exp(-3.6851 - 1360/T)$$

$$D_T \times 10^7 = 9.4 \times 10^{-3} T_{cg} - 1.75.$$

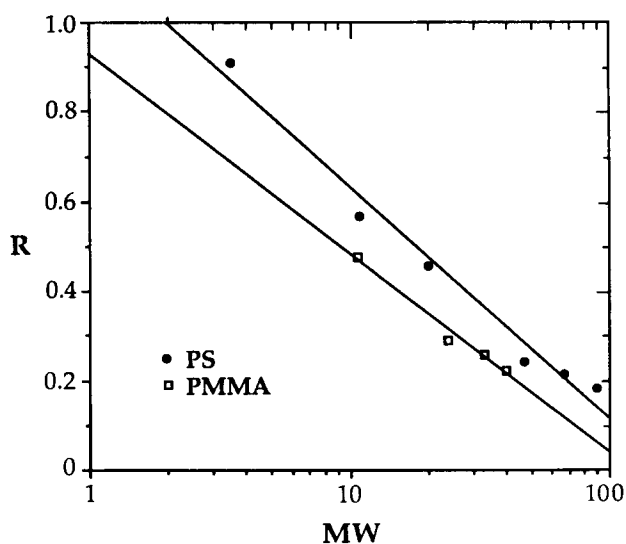


Figure 6 Normal calibration curve (R vs. $\log M$). Carrier was THF.

Table III Values of R and T_{cg} for PS in Different Solvents

Polymer-Solvent	$M \times 10^{-3}$	R	T_{cg} ($^\circ\text{C}$)
PS-THF	35	0.910	28.07
	110	0.568	25.79
	200	0.457	25.05
	470	0.241	23.61
	670	0.214	23.43
	900	0.184	23.23
PS-Toluene	35	0.750	27.28
	100	0.501	25.85
	200	0.392	25.00
	470	0.190	23.46
	670	0.175	23.35
	900	0.156	23.04
PS-MEK	35	0.744	26.96
	110	0.527	25.51
	200	0.417	24.78
	470	0.241	23.61
670	0.197	23.31	

In lieu of data for ethylbenzene, we estimated the variation of D and D_T at the lowest and highest T_{cg} obtained for PS in THF, namely, at 296.23 and 300.19°K , and found that the relative variations in D and D_T are 6.0 and 3.4% , respectively. Since, according to eq. (4), D_T is in the denominator and D is in the numerator of the expression for retention parameter l , the influence of temperature on retention is attenuated to a great extent, making the procedure reasonably reliable.

Frequently, it is difficult to obtain good molecular-weight standards for each polymer type that might

Table IV Values of R and T_{cg} for PMMA and P α MS in Different Solvents

Polymer-Solvent	$M \times 10^{-3}$	R	T_{cg} ($^\circ\text{C}$)
PMMA-THF	107	0.478	25.17
	240	0.289	23.93
	330	0.259	23.73
	400	0.224	23.49
PMMA-Toluene	107	0.267	23.78
	240	0.187	23.24
	330	0.156	23.04
PMMA-MEK	107	0.433	24.89
	240	0.297	23.89
	330	0.248	23.65
	400	0.222	23.48
P α MS-Toluene	139	0.356	24.37
	380	0.220	23.48

be in need of characterization. From the above discussion, it is clear that accurate universal calibration curves may be obtained using PS, PMMA, or other polymers for which standards are readily available. The necessary Mark-Houwink parameters a and k are listed in *Polymer Handbook*¹³ and other literature for these and numerous other polymers in a variety of solvents, which should facilitate the use of this procedure. The one parameter somewhat problematical is D_T since, at this point, thermodiffusion has been studied in only a small number of polymer-solvent systems.^{7,8} However, if one can access one or two samples of a given polymer for which the molecular weight is accurately known, it is possible to determine D_T for this material in a given solvent using the universal calibration procedure. Once D_T values for this and other systems are known, one can then utilize the desirable TFFF features of high resolution over a broad molecular-weight range.¹⁴

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