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Thermal Diffusion of Polystyrene in Eight Solvents by an Improved Thermal Field-Flow Fractionation Methodology[1]

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ABSTRACT: The characteristics and advantages of the thermal field-flow fractionation methodology for measuring thermal diffusion parameters in polymer solutions is discussed. The theory of the method is presented and is extended to include the effect of variable thermal conductivity. This in combination with experimental retention data yield values for thermal diffusion factors, α. To get thermal diffusion coefficient D_T, ordinary diffusion coefficient D is needed; Flory's method is used for this purpose. These parameters are acquired from experimental data obtained with polystyrene samples of molecular weight 20 000, 51 000, 97 000, and 160 000, dissolved in eight organic solvents. Trends occurring with changes in molecular weight, solvent, and temperature are investigated. Some aqueous solutions of macromolecules are shown to exhibit much weaker thermal diffusion effects.

Thermal field-flow fractionation (TFFF) comprises a methodological subclass of field-flow fractionation (FFF), a macromolecular separation technique.[2-5] In TFFF, a thermal gradient, applied across a channel through which solvent is flowing, retards the downstream progress of macromolecular solutes.[6-10] This retardation, or retention, is caused by thermal diffusion, which forces macromolecules into the low-velocity region next to the channel wall. Retention among assorted macromolecules is differential, hinging on the magnitude of the thermal diffusion effect for each species.

Differential retention causes separation and thus leads to the realization of the primary goal of TFFF: chemical fractionation. Differential retention also makes it possible to discern the magnitude of the underlying thermal diffusion effect, thus making it possible to measure thermal diffusion parameters for various macromolecules. This is an important secondary goal for TFFF, especially in view of the fact that existing data on thermal diffusion for macromolecules are scarce and inconsistent. In an earlier work it was shown that TFFF has certain advantages in making such measurements compared to other techniques, including those using thermogravitational columns, static cells, and moving boundaries.[11] These advantages include relative speed, simultaneous fractionation, and minute sample requirements (on the order of 1 mg).

In this paper we present an improved methodology for TFFF measurements and analyze the faults of the previous TFFF system. We introduce an important theoretical correction, accounting for the variation with temperature of solvent thermal conductivity. We report thermal diffusion parameters for a variety of chemical systems not yet characterized with respect to thermal diffusion. We analyze the results in an attempt to isolate the effects of temperature, molecular weight, and other chemical factors. Systems included in this study are polystyrene polymers of molecular weights 20 000, 51 000, 97 000, and 160 000, and solvents that include toluene, ethyl benzene, methyl ethyl ketone, chloroform, ethyl acetate, cyclohexane, dioxane, and dimethyl formamide. We also include some preliminary remarks on thermal diffusion (or the lack of it) in aqueous solutions and in binary mixtures of water with DMSO, urea, and guanidine hydrochloride.

Theory

The theory of TFFF has been developed and refined in several publications.[2b,3,8,9] The essential equations are based on the existence of an exponential steady-state solute cloud at the cold wall of the channel

$$c^* = c_0 \exp(-x/l) \tag{1}$$

In this equation, c^* is the steady-state concentration, c_0 the concentration at the cold wall, $x = 0$, and l is the characteristic thickness of the solute layer. Parameter l is most conveniently expressed in dimensionless form

$$\lambda = l/w \tag{2}$$

where w is the distance between hot and cold walls. In dilute solutions, which we assume here, quantity λ is related to thermal diffusion by[8]

$$\lambda = 1/\left(\frac{\alpha}{T} + \gamma\right)\frac{dT}{dx}w \tag{3}$$

where α is the thermal diffusion factor, γ is the (cubical) coefficient of thermal expansion of the solution, and dT/dx is the temperature gradient.

$$R = \frac{\frac{2\lambda\beta}{1-\beta\lambda}[(\beta\lambda + \beta - 1)\exp(\beta - 1/\lambda) + \beta\lambda - \beta - 1] + 2\lambda\beta[\exp(-1/\lambda) + \exp\beta]}{[1 - \exp(-1/\lambda)][(\beta - 2)\exp\beta + \beta + 2]} \tag{4}$$

The evaluation of α parameters under various circumstances hinges on the availability of reliable λ values. The latter are acquired through the measurement of solute retention in TFFF. The essential equation is eq 4 where R is the retention parameter, measured as the ratio of the elution time of an unretained peak to that of the solute peak in question. Quantity β is equal to $B\Delta T/T_c^2$, where ΔT is the temperature drop across the channel, T_c is the cold-wall temperature, and B is the exponential term fixing the temperature dependence of viscosity, η ($\eta = \eta_0 \exp(B/T)$). When β is small, R reduces to the isoviscous form applicable to most other methods of field-flow fractionation

$$R = 6\lambda[\coth(1/2\lambda) - 2\lambda] \tag{5}$$

Equation 4, by contrast, is corrected to account for viscosity variations in the system.

The basic sequence, then, is to measure R by means of experimental TFFF, to obtain λ from R using either eq 4 or 5, and finally to obtain α from λ using eq 3. However, the application of eq 3 is not straightforward as we now show.

Ideally the temperature gradient, $\mathrm{d}T/\mathrm{d}x$, would be constant across the channel and readily calculable. In fact, however, thermal conductivity varies sufficiently over the typical temperature increment of TFFF that the temperature profile becomes nonlinear. The corrections necessary to handle this nonlinearity are developed next.

Correction for Nonlinear Temperature Profile

When thermal conductivity is constant, $\mathrm{d}T/\mathrm{d}x$ is constant across the channel, and may be replaced by $\Delta T/w$. Hence we have

$$\lambda = 1\Big/\left(\frac{\alpha}{T} + \gamma\right)\Delta T \tag{6}$$

However, with a variable thermal conductivity, $\mathrm{d}T/\mathrm{d}x$ varies. It is then necessary to choose an appropriate value for $\mathrm{d}T/\mathrm{d}x$ to be used in eq 3. In most practical cases of TFFF, the solute cloud hugs the cold wall. The cold wall value of $\mathrm{d}T/\mathrm{d}x$, $(\mathrm{d}T/\mathrm{d}x)_c$, may therefore be used to good approximation. This approximation can be refined somewhat by replacing $\mathrm{d}T/\mathrm{d}x$ by the value of the temperature gradient at the center of gravity of the solute cloud, $(\mathrm{d}T/\mathrm{d}x)_{cg}$.

The necessary values for $\mathrm{d}T/\mathrm{d}x$ can be approximated as follows. We assume that the thermal conductivity, k, varies linearly with temperature: $k = k_c + (\mathrm{d}k/\mathrm{d}T)(\delta T)$, where $\mathrm{d}k/\mathrm{d}T$ is constant. The temperature gradient, $(\mathrm{d}T/\mathrm{d}x) = A/k$, then appears as

$$\mathrm{d}T/\mathrm{d}x = A/[k_c + (\mathrm{d}k/\mathrm{d}T)(\delta T)] \tag{7}$$

Integration from the cold wall ($x = 0$, $T = T_c$) gives

$$\delta T + \frac{1}{k_c}\frac{\mathrm{d}k}{\mathrm{d}T}\frac{(\delta T)^2}{2} = Ax \tag{8}$$

Constant A is definable in terms of heat flux, but is more convenient in experimental terms to relate A to total channel temperature drop, ΔT. This can be done by noting that $\delta T = T - T_c$ must equal ΔT at $x = w$. With the resulting A value substituted above, we have

$$\delta T + \frac{1}{k_c}\frac{\mathrm{d}k}{\mathrm{d}T}\frac{(\delta T)^2}{2} = \left(\Delta T + \frac{1}{k_c}\frac{\mathrm{d}k}{\mathrm{d}T}\frac{(\Delta T)^2}{2}\right)\frac{x}{w} \tag{9}$$

This equation yields a temperature gradient, $(\mathrm{d}T/\mathrm{d}x) = \mathrm{d}(\delta T)/\mathrm{d}x$, of the form in eq 10.

$$\frac{\mathrm{d}T}{\mathrm{d}x} = \frac{\frac{\Delta T}{w} + \frac{1}{k_c}\frac{\mathrm{d}k}{\mathrm{d}T}\frac{(\Delta T)^2}{2w}}{1 + \frac{1}{k_c}\frac{\mathrm{d}k}{\mathrm{d}T}\delta T} \tag{10}$$

Expansion of the denominator in the form of $1/(1 + x) \cong 1 - x$, along with the elimination of higher order terms, yields the simple approximate equation

$$\frac{\mathrm{d}T}{\mathrm{d}x} = \frac{\Delta T}{w}\left[1 - \frac{1}{k_c}\frac{\mathrm{d}k}{\mathrm{d}T}(T - \bar{T})\right] \tag{11}$$

where $\bar{T}$ is the mean channel temperature, $(T_H + T_c)/2$.

At the cold wall ($\delta T = 0$), the temperature gradient, according to either of the last two equations, is

$$\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)_c = \frac{\Delta T}{w} + \frac{1}{k_c}\frac{\mathrm{d}k}{\mathrm{d}T}\frac{(\Delta T)^2}{2w} \tag{12}$$

From eq 3 and the excellent approximation that the zones center of gravity occurs at characteristic distance l,[8] we can surmise that the δT value at the zone's center of gravity is $l(\mathrm{d}T/\mathrm{d}x)_{cg}$, or

$$(\delta T)_{cg} = 1\Big/\left(\frac{\alpha}{T} + \gamma\right) \tag{13}$$

which gives a corresponding gradient of

$$\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)_{cg} = \frac{\frac{\Delta T}{w} + \frac{1}{k_c}\frac{\mathrm{d}k}{\mathrm{d}t}\frac{(\Delta T)^2}{2w}}{1 + \frac{1}{k_c}\frac{\mathrm{d}k}{\mathrm{d}T}\frac{1}{[(\alpha/T) + \gamma]}} \tag{14}$$

Either of these can be used in eq 3, depending on circumstances. When $(\mathrm{d}T/\mathrm{d}x)_c$ is used, eq 6 becomes

$$\lambda = 1\Big/\left(\frac{\alpha}{T} + \gamma\right)\Delta T\left(1 + \frac{1}{k_c}\frac{\mathrm{d}k}{\mathrm{d}T}\frac{\Delta T}{2}\right) \tag{15}$$

The correction factor with respect to eq 6, marking the approximate departure of λ from its value for constant thermal conductivity, is seen to be

$$\lambda/\lambda(\text{const } k) = 1\Big/\left(1 + \frac{1}{k_c}\frac{\mathrm{d}k}{\mathrm{d}T}\frac{\Delta T}{2}\right) \tag{16}$$

Table I shows the magnitude of various terms in this correction factor for solvents used in this study. At $\Delta T = 60$ °C, the factor of eq 16 yields a correction of roughly 3% in λ and thus in α.

The more exact treatment used here to obtain our quantitative results involves substituting eq 14 into eq 3. The resulting quadratic equation can be solved to yield the following explicit equation for α.

$$\alpha = (T/2)(Q - 2\gamma + \{Q^2 + (4Q/k_c)\,\mathrm{d}k/\mathrm{d}T\}^{1/2}) \tag{17}$$

$$\text{where } Q = 1/\lambda\Delta T[1 + (\Delta T/2k_c)\,\mathrm{d}k/\mathrm{d}T]$$

This equation has been used in the present computation of α values. The value of λ, of course, must be extracted from experimental results using eq 4.

Finally, the form of $\mathrm{d}T/\mathrm{d}x$, calculated from eq 9, is shown in Figure 1. The example shown in this figure is a rather extreme one, applicable to a 100 °C drop across ethylbenzene solvent.

We note here that the exponential distribution of eq 1,

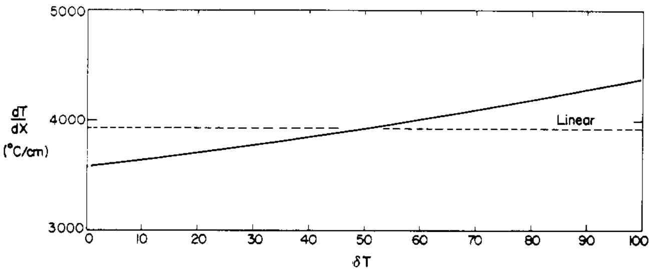

Figure 1. Variation of temperature gradient in the channel as a function of temperature increment, δT, above the cold-wall temperature, T_c, for ethylbenzene. $T_c = 0$ °C; $\Delta T = 100$ °C.

Table I
Value of Terms Involved in the Correction for Nonconstant Thermal Conductivity and for Thermal Expansion
(Values of k at 293°C)

Solvent	$k \times 10^4$, cal (s cm °C)	$-(\mathrm{d}k/\mathrm{d}T) \times 10^7$, k/°C	$\frac{1}{2k}\frac{\mathrm{d}k}{\mathrm{d}T} \times 10^4$, 1./°C	$\gamma \times 10^4$, 1./°C	Ref
Ethylbenzene	3.16	5.83	9.22		12
Toluene	3.24	5.92	9.13		13
	3.24	6.06	9.35		14
				11.4	15
Chloroform	2.85	6.69	11.7		12
				7.3	16
Ethyl acetate	3.63	12.0	16.5		12,17
Cyclohexane	2.89	6.02	10.4		19
	2.96	7.75	13.1		18
Dimethyl formamide	4.48	6.14	6.85		13
2-Butanone (MEK)	3.50	5.42	7.74	16.0	20
	3.74	12.6	16.8		18
				12.6	21
Dioxane	3.68[a]				22

[a] Temperature not given.

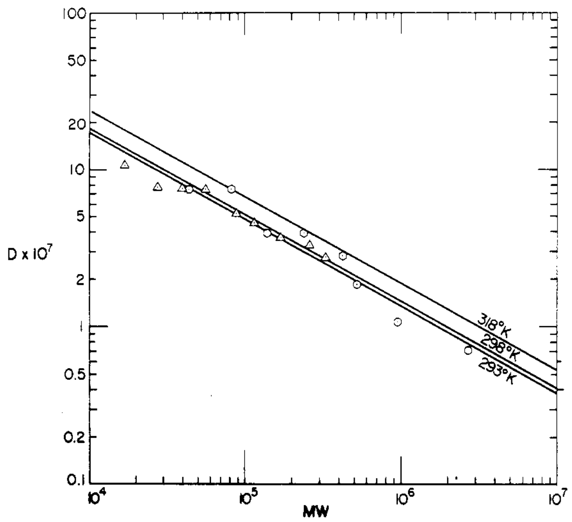

Figure 2. Comparison of diffusion coefficients predicted by eq 20 and experimental values for polystyrene of various molecular weights in toluene. (○) Meyerhoff and Nachtigal, 293 °K;[29] (△) Bugdahl, 298 °K;[30] ○ Taylor, 318 °K.[31]

upon which all the subsequent theory hinges, is valid only if λ (or l) is constant over the depth of the solute cloud. Clearly this is not rigorously so: (α/T), γ, and $\mathrm{d}T/\mathrm{d}x$ will all vary slightly with temperature. We assume that these variations will have only a small effect on retention. These variations will be especially insignificant for highly retained solutes which have small l and λ values, and which thus extend over only a small temperature interval. High retention is a goal sought in the practical uses of TFFF. In this study λ values rarely exceed 0.15, and most are smaller.

Method for Calculating Diffusion and Thermal Diffusion Coefficients

Equation 17 leads us directly to values for the thermal diffusion factor, α. In order to calculate values for the coefficient of thermal diffusion, D_T, use must be made of the equation defining α,[23]

$$\alpha = D_T T/D \tag{18}$$

and means must be found for estimating the value of the ordinary coefficient of diffusion, D. We have proceeded as follows.

Diffusion coefficient D is best written in terms of the friction coefficient for molecular transport, f, using the Einstein relationship, $D = kT/f$, applicable to dilute solutions.[24] Flory has dealt extensively with factors influencing f.[25] Based on his treatment we have computed friction coefficients for polystyrene at infinite dilution in a series of solvents. Flory gives the following expression

$$f_0/\eta_0 = 5.11(\overline{r_0^2}/M)^{1/2}M^{1/2}\alpha' \tag{19}$$

where at the theta temperature the ratio between mean square end-to-end distance, $\overline{r_0^2}$, and molecular weight, M, is independent of molecular weight and thus assumes a characteristic value for each type of polymer. This ratio varies only slowly with temperature (down 3.5% from 25 to 70 °C for polystyrene in toluene) and shows very little dependence on solvent. We have used the value 722×10^{-11} for $(\overline{r_0^2}/M)$ throughout. Parameter α', the solvent–solute interaction parameter, does show a distinctive temperature dependence

$$\alpha'^5 - \alpha'^3 = 2C_M\psi\left(1 - \frac{\theta}{T}\right)M^{1/2}$$

where C_M is an aggregate term, nearly independent of temperature, introduced by Flory, and ψ is an entropy of dilution term. The product ψC_M has been determined through intrinsic viscosity studies of polystyrene in a variety of solvents.[26,27] Based on these data together with the temperature dependence of solvent viscosities available in standard handbooks and in the book by Reid and Sherwood,[28] we have computed friction coefficients and from them diffusion coefficients through $D = kT/f$.

Diffusion coefficients calculated by this method can be closely approximated (within 1% for ethylbenzene) by the equation

$$D = (\text{mol wt})^A \exp\left(B + \frac{C}{T}\right) \tag{20}$$

where A, B, and C are −0.552, −3.685 1, and −1 360, respectively, for ethylbenzene; and −0.553, −3.802 9, and −1 285, respectively, for toluene. Figure 2 compares experimental diffusion coefficients[29,30,31] for polystyrene in toluene and those calculated by the above relation. The experimental points are for data extrapolated or reported for zero concentration. Comparable agreement is found for data on ethylbenzene[32] and cyclohexane[33] solvents.

Experimental Section

The TFFF apparatus and operating procedure have been described previously.[9] Injection by the stop-flow method was used for the ethyl benzene experiments, while injections were made directly into the flowing solvent in all other cases. Ultra-narrow polystyrene fractions ($M_w/M_n < 1.009$) supplied by Waters Associates were used in the ethylbenzene studies. Polystyrene fractions ($M_w/M_n < 1.06$) supplied by Pressure Chemical Co. were utilized

Table II
Values of α and D_T for Various Solvents, Molecular Weights, and Temperature Increments

Polystyrene mol wt	Solvent	T_{cg}, K	ΔT, K	α^a	α_{uncorr}	$D \times 10^7$, cm²/s⁻¹	$D_T \times 10^7$, cm²/s⁻¹ K⁻¹
19 800	Toluene	302.5	32	25.8 ± 0.7	25.6 ± 0.7	13.3	1.13
		302.5	19	29.8 ± 1.5		13.3	1.31
	Ethyl acetate	303.4	33	22.4	22.2	19.2	1.42
	2-Butanone (MEK)	301.9	32	29.0 ± 1.9	28.8 ± 1.9	20.5	1.97
	p-Dioxane	302.7	31		24.3	6.83	0.55
	Cyclohexane	299.9	20	29.6	29.6	9.12	0.90
		303.8	38	23.6	23.7	9.86	0.77
	Dimethylformamide	299.9	30	22.3 ± 2.1	22.2 ± 2.1		
51 000	Toluene	299.0	30	48.3 ± 1.6	47.5 ± 1.6	7.56	1.22
		298.5	19	44.5 ± 2.2	44.3 ± 2.1	7.51	1.12
	Ethyl acetate	300.5	33	38.8	37.6	11.3	1.46
	2-Butanone (MEK)	299.3	32	46.5 ± 2.6	45.5 ± 2.5	12.3	1.91
	p-Dioxane	299.5	31		43.9	3.85	0.564
	Cyclohexane	298.9	20	42.0 ± 2.8	42.0 ± 2.8	5.62	0.790
	Dimethylformamide	297.9	30	33.3 ± 1.6	33.0 ± 1.6		
	Chloroform	300.6	22	27.0 ± 2.3	27.0 ± 2.2		
97 200	Toluene	297.5	32	66.0 ± 0.7	64.6 ± 0.6	5.18	1.15
		297.2	19	66.5 ± 1.4	65.9 ± 1.4	5.16	1.15
	Ethyl acetate	297.9	33	62.7	60.2	7.92	1.67
	2-Butanone (MEK)	297.8	32	64.0	62.0	8.51	1.83
	p-Dioxane	297.6	31		64.0	2.64	0.568
	Cyclohexane	298.1	30	58.6 ± 5.8	57.4 ± 5.6	4.10	0.806
	Dimethylformamide	295.9	30	49.2 ± 2.6	48.6 ± 2.6		
	Chloroform	298.8	22	43.7 ± 5.5	43.3 ± 5.3		
160 000	Toluene	296.3	32	93.1 ± 2.6	90.8 ± 2.5	3.86	1.21
		296.4	19	87.4 ± 1.0	86.4 ± 1.0	3.86	1.14
	Ethyl acetate	297.2	33	73.4	70.4	5.93	1.46
	2-Butanone (MEK)	296.3	32	95.5 ± 8.2	93.6 ± 8.0	6.48	2.09
	p-Dioxane	296.6	31		83.2	1.98	0.555
	Dimethylformamide	297.5	30	66.6 ± 4.5	65.6 ± 4.4		
	Chloroform	297.6	20	55.6 ± 1.3	60.3 ± 1.4		

[a] Three or more measurements for each value followed by a standard deviation; one measurement for all others. The thermal expansion term, γ, is ignored; it is responsible for an increment of only about 0.3 units in α.

in all the other solvents. Polystyrene samples consisted of 0.2 mg of polystyrene in 10 μl of toluene solution. Blue Dextran (mol wt approximately 2 × 10^6) supplied by Pharmacia was used in the DMSO studies. All solvents and other chemicals used were reagent grade. The channel thickness, w, was 0.0254 cm for the ethylbenzene and DMSO studies, and 0.0127 cm for the other experiments. DMSO chemically attacked the copper surfaces, necessitating the use of the gold-plated copper-bar system for studies with this solvent.[9]

Results and Discussion

The principal results of this investigation, which bear on solvent effects in association with molecular weight, are reported in Table II. Values reported for the thermal diffusion factor, α, were obtained from eq 17. Polymer diffusion coefficients, D, were obtained at the characteristic (center-of-gravity) temperature by Flory's method. With these values, thermal diffusion coefficient D_T was calculated by using $D_T = \alpha D/T_{cg}$, obtained from eq 18. We also report a value for α_{uncorr}, a value in which α is computed without benefit of the correction for nonuniform temperature gradient.

The trend in α for different solvents with changes in polymer molecular weight is shown in Figure 3. Despite the wide range of solvent types, α values are seen to lack wide variation. Ethylbenzene invokes the largest thermal diffusion effect (largest α) while chloroform induces the least. Correlations have been sought between the magnitude of α and various solvent and interactive parameters such as θ temperatures, dipole moments, Hildebrand solubility parameters, molecular weight, and molecular size. No significant trends are evident, except perhaps in molecular volume. There is a general increase in α with molar volume, although the increase is not smooth and uniform. We are unaware of any detailed theory which would suggest other parameters for possible correlation.

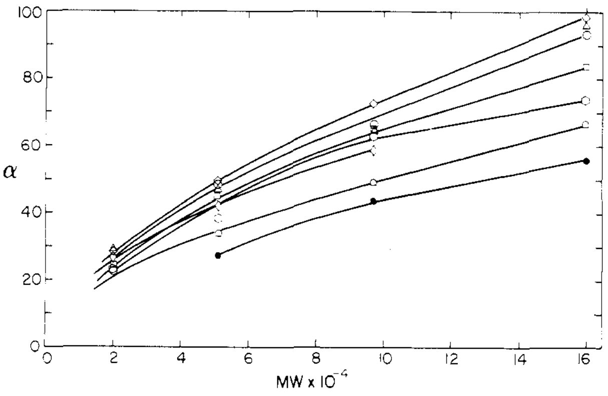

Figure 3. Values of thermal diffusion factor, α, plotted against the molecular weight of polystyrene in various solvents: (○) toluene; (○) ethyl acetate; (△) 2-butanone (MEK); (□) *p*-dioxane; (◊) cyclohexane; (▢) dimethylformamide; (●) chloroform; (◇) ethylbenzene.

With regard to polymer molecular weight, α values show a consistent upward trend, as shown in Figure 3. (This figure includes an ethylbenzene curve derived from data in Table III.) The various solvents retain their levels of thermal diffusion relative to one another through this eightfold range in molecular weight, with only a few minor exceptions.

In order to ascertain the effect of temperature on α, the ultra-narrow polystyrene fractions were each subjected to a series of experiments in ethylbenzene using different cold-wall temperatures, and thus different effective temperatures, T_{cg}. Table III reports these data. Figure 4 shows that

Table III
Values of α and D_T for Polystyrene in Ethylbenzene at Various Effective Temperatures, T_{cg} (ΔT = 40°C)

Polystyrene mol wt	T_c, K	T_{cg}, K	α	α_{uncorr}	$D \times 10^7$, cm^2 s^{-1}	$D_T \times 10^7$, cm^2 s^{-10} K^{-1}
20 000	270	278.3	32.7 ± 0.6	32.0 ± 0.6	8.00	0.940
	303	313.3	27.2 ± 0.1	26.8 ± 0.1	13.8	1.20
	333	346.0	19.9 ± 0.9	19.8 ± 0.8	20.8	1.20
51 000	270	275.0	56.2 ± 3.0	54.7 ± 2.9	4.50	0.920
	308	315.1	44.4 ± 1.5	43.3 ± 1.4	8.44	1.19
	333	341.9	36.7 ± 0.8	35.9 ± 0.7	11.8	1.27
97 000	270	273.2	86.9 ± 2.0	84.3 ± 2.0	3.05	0.970
	303	307.5	70.5 ± 1.0	68.4 ± 0.9	5.32	1.22
	333	339.4	53.7 ± 1.6	53.7 ± 1.5	8.07	1.28
160 000	270	272.5	113.9 ± 0.8	110.4 ± 0.7	2.29	0.957
	303	306.2	97.9 ± 5.4	94.7 ± 5.2	3.96	1.27
	333	337.9	70.7 ± 2.0	68.5 ± 1.9	6.01	1.26

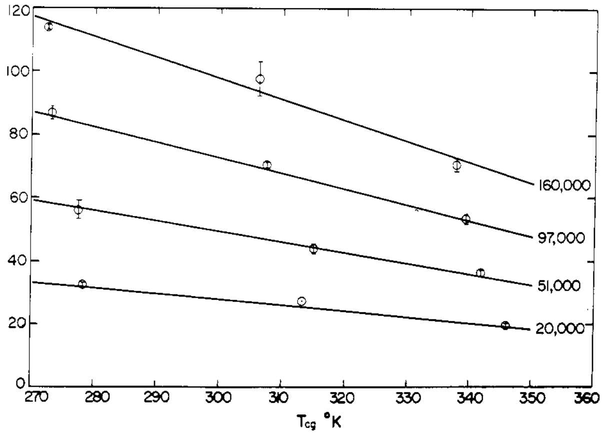

Figure 4. Variation of α with center-of-gravity temperature, T_{cg}. Vertical bars indicate standard deviations; where no vertical bars appear the standard deviation is less than the circle diameter. Each point represents the average of three to ten measurements.

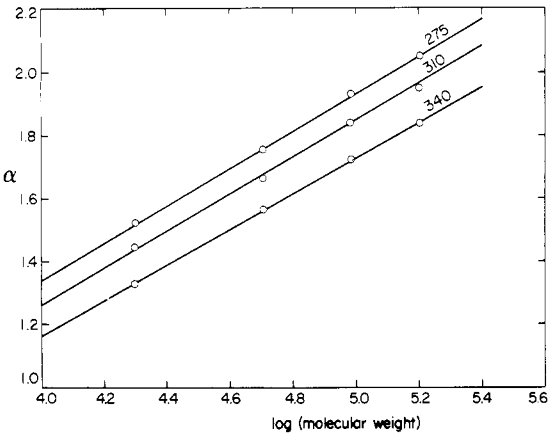

Figure 5. Log α vs. log mol wt at different temperatures, T_{cg}. From top line to bottom, T_{cg} = 280, 310, and 340 °K, respectively. The corresponding slopes, obtained by least squares, are 0.595, 0.587, and 0.568, respectively.

the variation of α with temperature is nearly linear over the range studied. The solid lines of the figure are all calculated from the single empirical equation

$$\alpha = (\text{mol wt})^{0.6}\left(\frac{1}{4.47} - \frac{T_{cg}}{2000}\right) \quad (21)$$

This equation shows good accord with the data, as can be seen from the figure.

Equation 21 suggests that a plot of log α vs. log mol wt would yield a straight line. This, in fact, applies with very little deviation over the eightfold range of polymer molecular weight, as Figure 5 demonstrates. In this figure, effective temperatures, T_{cg}, were reduced to common values by extrapolation from nearby points using the temperature trend suggested by eq 21. The average value of the least-squares slopes of these three lines is 0.583.

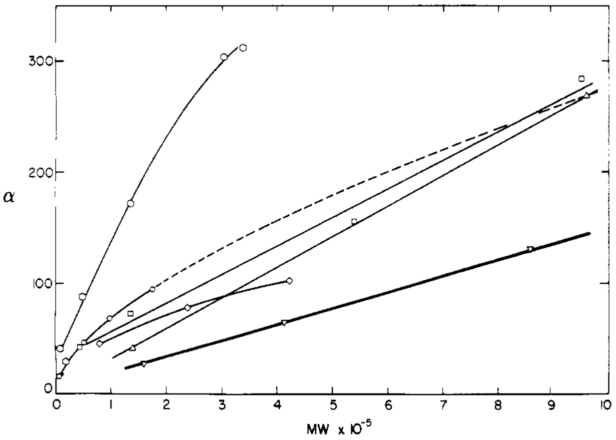

Figure 6. Thermal diffusion factor vs. molecular weight for polystyrene in toluene: (△) Meyerhoff and Rauch, 293 °K;[34] (○) Emery and Drickamer, 298 °K;[35] (□) Meyerhoff and Nachtigall, 298 °K;[29] (◇) Taylor, 318 °K;[31] (▽) previous work in this laboratory, 313 °K;[11] (○) present work, 310 °K, dotted line was calculated from eq 21.

It is difficult to verify the above values of α and conclusions in an absolute sense because the limited literature results on these solute–solvent systems disagree with one another significantly. Few of them entail low solute concentrations, and extrapolations to zero concentration must be made. The problems are illustrated in Figure 6. The details involved in the construction of this type of figure are provided in the earlier publication.[11] The solvent reported in that figure is toluene inasmuch as insufficient data exist for other solvents. The present results agree in general with literature values of Figure 6, but the uncertainties in the latter are as large as a factor of 4 in magnitude.

Unfortunately our present results also disagree with previous results from this laboratory, as the figure illustrates.[11] We have looked at this matter carefully, and feel that the error belongs to the earlier methodology, which was much more primitive. The earlier apparatus consisted of two 2.54-cm square tubes separated by a Teflon spacer. The temperature increment, ΔT, was taken as that existing between the heat exchange media flowing in the tubes: hot oil and cold water. This procedure neglected that part of the total temperature drop taken up by the 0.254-cm stainless steel wall and by the adjacent boundary layers of circulating coolant. The actual ΔT was apparently less than that recorded, and this led to the undervaluation of α's. When

Table IV
Effect of Different Temperature Increments, ΔT, on Polystyrene Retention Ratio, R, and Thermal Diffusion Factor, α[a]

Polystyrene mol wt	ΔT, K	R	T_{cg}, K	α	
5 000	80	0.822	310.8	12.3	12.0 ± 1.5
	60	0.913	309.5	10.4	
	40	0.937	303.4	13.4	
20 000	80	0.579	301.0	24.8	26.1 ± 1.4
	60	0.685	300.3	25.8	
	40	0.803	298.8	27.6	
51 000	80	0.376	295.8	44.8	44.4 ± 1.4
	60	0.473	295.6	44.8	
	40	0.632	295.4	45.6	
	20	0.875	294.8	42.4	
97 000	80	0.263	293.5	64.6	67.3 ± 4.5
	60	0.333	293.0	72.7	
	40	0.470	293.2	69.2	
	20	0.774	293.4	62.7	
160 000	80	0.171	291.8	102.7	98.5 ± 5.6
	60	0.236	291.9	100.9	
	40	0.349	291.9	100.0	
	20	0.643	292.2	90.2	

[a] Cold-wall temperature T_c is 16°C for all experiments. Solvent is ethylbenzene.

such ΔT corrections are made, most of the apparent differences disappear. The present copper plate systems utilize thermistors inserted within 0.08 cm of the copper–solvent interface. These systems have given excellent reproducibility with four different columns, some of different dimensions, yielding values of R within ±0.02, while the earlier system yielded a range of ±0.15 for R values.

In further confirmation of the reproducibility of our results under different experimental conditions, we have applied several different temperature increments to each polystyrene fraction, checking to see if α values remain constant. The results are shown in Table IV. Although retention ratio R varies significantly for each polymer, the α values derived from R, except for fluctuations, appear to remain independent of ΔT, as desired.

Values of D_T are shown also in Tables II and III. Inspection shows that there is no definitive molecular weight dependence to D_T. This is in agreement with earlier observations. However, a slight increase of D with molecular weight is suggested. This is confirmed by noting that α and D apparently have slightly different than reciprocal molecular weight dependencies, expressed respectively by eq 21 and 20. The dependence of D_T, as shown by eq 18, is governed by the product of the two. The sum of the exponents associated with molecular weight in α and D is $0.600 - 0.552 = 0.048$ using eq 21 or $0.583 - 0.552 = 0.031$ using the least-square value for α's in ethylbenzene. A combination of experimental uncertainties and the approximate nature of the Flory treatment dictate that these residual exponents be used cautiously. The subject merits further investigation.

If one assumes the absence of a molecular weight effect, the average D_T applicable to each solvent is 1.2×10^{-7}, 1.6×10^{-7}, 1.9×10^{-7}, 0.60×10^{-7}, and 0.92×10^{-7} cm^2 s^{-1} K^{-1} for toluene, ethyl acetate, MEK, dioxane, and cyclohexane, respectively, at $T_{cg} = 300 \pm 5$ K. The low D_T and D values in dioxane and cyclohexane reflect the high viscosities of these solvents. A number of workers[29,31,34,36-40] have given D_T values in the range $(1.0 \pm 0.5) \times 10^{-7}$ cm^2 s^{-1} K^{-1} for polystyrene in toluene in the region of 10–50 °C. These agree well with the value reported above.

The temperature dependence of D_T is striking, as shown by Figure 7. At first D_T rises rapidly with temperature, then at higher temperatures the growth trend disappears, and even reverses in one case. The solid lines in this figure are obtained by using $D_T = \alpha D/T$, eq 18, along with the two empirical equations, eq 20 and 21. A reversal occurs, but may not be meaningfully extrapolated beyond the highest temperature utilized experimentally.

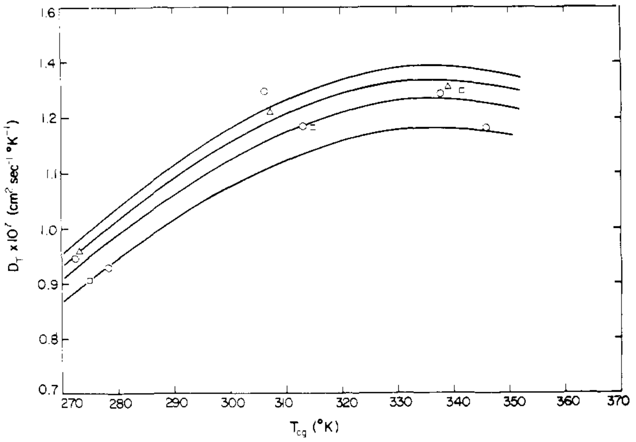

Figure 7. Thermal diffusion coefficient, D_T, for polystyrene in ethylbenzene as a function of effective temperature, T_{cg}, for different polymer molecular weights: (○) 20 000, (□) 51 000, (△) 97 000, (○) 160 000. Solid lines from combined empirical equations (see text).

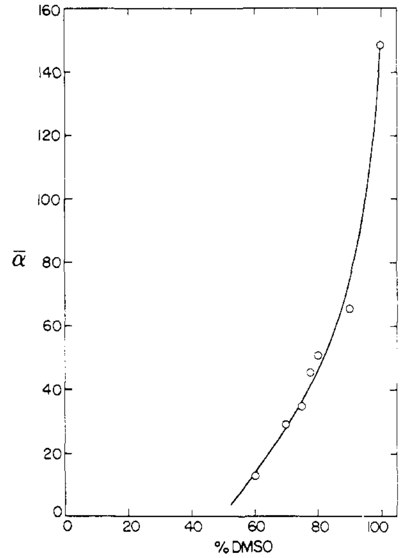

Figure 8. Thermal diffusion factor, α, for Blue Dextran (mol wt = 2×10^6) vs. volume percentage of DMSO in an aqueous solution with ΔT = 45 °K and T_c = 295 °K.

Attempts were also made to measure α values in aqueous systems using the gold-plated column. Blue Dextran, albumin (bovine serum), and hemoglobin (bovine) were run in various aqueous buffers as well as in 2 and 6 M guanidine hydrochloride and 8 M urea. No significant retention was detected, indicating very low thermal diffusion in these aqueous systems. Seelback[41] and Pawlowski[42] have reported separations of carbohydrates by thermal diffusion in aqueous solutions. However, Bonner[40] found no evidence for thermal diffusion of Blue Dextran T250 in water and salt solutions, placing an upper limit for thermal diffusion of these materials at least an order of magnitude less than that for polystyrene in toluene.

When sufficient diluent, for example, DMSO, is added to water, α's apparently became detectable. An example of this is shown in Figure 8. Here values of α for Blue Dextran of nominal molecular weight 2×10^6 are shown to first become observable at 60% DMSO.

These studies point up the dramatic contrast existing in solvent effects. Organic solvents appear remarkably similar in influence, as noted earlier. Yet with polar solutes, water appears to destroy nearly all vestiges of thermal diffusion. The effect is undoubtedly attributable to some aspect of solute–solvent interaction, perhaps the presence or absence of hydrogen bonding. Unfortunately, sufficient data do not exist, particularly in polymer systems, to discern clear solute–solvent trends. While the present study fills a wide gap in the study of solvent and temperature effects, an equally comprehensive study of different solute types is needed to arrive at definitive correlations regarding molecular structure factors in thermal diffusion.

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Aggregation of Polyion Complexes between Synthetic Polyelectrolytes

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ABSTRACT: Dissolving polyion complexes in the aqueous solution aggregate time dependently to a highly ordered fibrous structure. Poly(carboxylic acid)s and integral type polycations with quaternary ammoniums on their chain backbones are used as polyanion and polycation, respectively. The variety of the component poly(carboxylic acid) influences surface condition and diameter of fibrous aggregates and the chain lengths or rigidity of polycations change their basic shapes. Hydrophobic interaction is the main cause for the spontaneous aggregation of polyion complexes.

In biological systems, complicated and specific functionalities are caused by the regular molecular aggregation, for example, folding, renaturation, self-assembly, and so on. In recent years the studies of the higher-ordered structures of biopolymers have been developed remarkably. However, the general rule for molecular aggregation has not been established yet even in biological systems because of the complexity and specificity of biopolymers.

In comparison with biopolymers, synthetic polymers have simple structures. So they would have advantages over confirming and understanding the fundamental phenomena of the complicated reactions in vivo. For this reason, the study about the mechanisms of the complexations between synthetic macromolecules must give important suggestions to design the functions on polymer chains. Some works about the complexation through such secondary binding forces as van der Waals,[1] Coulombic force,[2,3] hydrogen bond,[4,5] and hydrophobic interaction have been reported. Such primary complexes obtained from the contact of synthetic component polymer chains take further aggregation with each other under particular conditions like biological systems.[6,7]

The authors have already reported the primary complexation mechanisms between oppositely charged synthetic polyelectrolytes (polyion complex). The compositions of the complexes are determined mainly by the degree of dissociation of component polyelectrolytes,[8] and each active site reacts cooperatively.[9] Moreover, they reported the phe-