Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Ko, Gwon-Hee , Richards, Robyn and Schimpf, Martin E.(1996) 'Enhanced Mass Selectivity in Thermal Field-Flow Fractionation Due to the Temperature Dependence of the Transport Coefficients', Separation Science and Technology, 31: 8, 1035 — 1044

To link to this Article: DOI: 10.1080/01496399608001332

URL: http://dx.doi.org/10.1080/01496399608001332

SEPARATION SCIENCE AND TECHNOLOGY, **31**(8), pp. 1035–1044, 1996

Enhanced Mass Selectivity in Thermal Field-Flow Fractionation Due to the Temperature Dependence of the Transport Coefficients

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ABSTRACT

Mass selectivity in thermal field-flow fractionation (ThFFF) is governed by the dependence of molecular weight M on the ratio of the diffusion coefficient D to the thermal diffusion coefficient D_T. Although studies indicate that D_T is independent of molecular weight in homopolymers (meaning that mass selectivity depends on differences in D alone), the greatest possible dependence of D on M predicted by polymer theory is not enough to account for the selectivity obtained in certain polymer–solvent systems. However, the increased selectivity can be explained by the temperature dependence of D/D_T. Thus, lower molecular weight polymers, which are less compressed against the cold wall, experience a higher mean temperature. Since values of D/D_T increase with temperature, the decrease in retention with M is greater than that predicted without considering the temperature dependence. We quantify the increased selectivity for polystyrene in ethylbenzene using a temperature-dependent value of D/D_T in the concentration profile. When the temperature dependence of D/D_T is removed, the selectivity decreases from 0.64_6 to 0.57_4. Although it does not constitute proof, the lower value is consistent with D_T being independent of M.

INTRODUCTION AND BACKGROUND

Thermal field-flow fractionation (ThFFF) is an analytical technique that separates polymers according to molecular weight (1–3). The technique, which is used to quantify the molecular weight distribution (MWD) of polymers, relies on the tendency of dissolved polymer components to "thermally" diffuse to the cold wall of the ThFFF channel.

The flux J_{th} of material due to thermal diffusion is defined phenomenologically by

$$J_{th} = cD_T(dT/dx) \tag{1}$$

where D_T is the thermal diffusion coefficient, c is concentration, and dT/dx is the temperature gradient across the channel (coordinate x). The buildup in concentration induces an opposing flux J_m, defined phenomenologically by Fick's law:

$$J_m = D(dc/dx) \tag{2}$$

Here, D is the ordinary (mass) diffusion coefficient and dc/dx is the concentration gradient formed by thermal diffusion. A dynamic steady-state is reached where the two opposing fluxes are balanced; this balance results in the following equation:

$$\frac{1}{c(x)}\frac{dc(x)}{dx} = -\frac{D_T}{D}\frac{dT(x)}{dx} \tag{3}$$

The concentration profile of a polymer component that has relaxed into its steady-state position at the cold wall is defined by rearranging Eq. (3) and solving the resulting differential equation. If D_T and D are assumed to be independent of temperature and concentration, the concentration profile is defined by

$$c(x) = c_0 \exp\left[-\frac{D_T}{D}(T(x) - T_c)\right] \tag{4}$$

where c_0 and T_c are the concentration and temperature at the cold wall, respectively. The concentration profile has a center of gravity that is defined by the following equation:

$$\int [c(x)\cdot x - c(x)\cdot l]\, dx = 0 \tag{5}$$

where l is the distance from the cold wall to the center of gravity of the zone, often referred to as the mean layer thickness of the zone. Rearranging Eq. (5) yields

$$l = \frac{\int [c(x)\cdot x]\, dx}{\int c(x)\, dx} \tag{6}$$

Combining Eqs. (4) and (6) yields the following dependence of l on the field strength and transport coefficients:

$$l = \frac{D}{D_T}\frac{1}{dT/dx} \tag{7}$$

Assuming laminar flow and a constant viscosity across the channel, parameter l can also be related to the volume V_r of carrier liquid required to elute a polymer zone having a concentration profile defined by Eq. (4):

$$R = \frac{V^0}{V_r} = 6\frac{l}{w}\left[\coth\left(\frac{w}{2l}\right) - 2\frac{l}{w}\right] \tag{8}$$

Here R is termed the retention ratio, V^0 is the geometric volume of the channel, and w is the channel thickness. In ThFFF, Eq. (8) must be corrected for the temperature dependence of the viscosity and thermal conductivity, which skews the velocity profile. [The corrections are lengthy and can be found elsewhere (4, 5).] Nevertheless, for a given set of experimental conditions, differences in V_r with molecular weight M arise from differences in D/D_T.

The dependence of D on molecular weight takes the following general form (6):

$$D = AM^{-b} \tag{9}$$

where A and b are constants. Studies by Schimpf et al. (7, 8) indicate that D_T is independent of M, at least for homopolymers. Insertion of Eq. (9) into Eq. (7) yields the following dependence of l on M when characterizing the MWD of a homopolymer by ThFFF:

$$l = CM^{-b} \tag{10}$$

Here, the constant $C = A/[D_T(dT/dx)]$ assumes a uniform field and constant value of D_T. For the purpose of this study, we define selectivity s_l as

$$s_l = \left|\frac{d \ln l}{d \ln M}\right| = \left|\frac{d \ln D}{d \ln M}\right| = b \tag{11}$$

In the limit of high retention (small l), s_l is equivalent to the more commonly used mass selectivity S_m, defined by (3)

$$S_m = \left|\frac{d \ln V_r}{d \ln M}\right| \tag{12}$$

Flory (9) used mean-field theory to set a maximum value of 0.60 for b. This value, which is expected for a polymer dissolved in an ideal solvent, was modified by de Gennes (10) to 0.585 using renormalization group theory. However, values of b as high as 0.65 have been reported in the literature (11) using nonisoviscous corrections to Eq. (8) in calculating l values. Furthermore, ThFFF experts generally agree that for polystyrene in ethylbenzene, empirically determined values of S_m and s_l are consistently above 0.6. Such reports have led to speculation that D_T has a slight dependence on M (12). Our objective in this work is to show that the additional selectivity is not necessarily due to a molecular weight dependence of D_T, rather it can be accounted for by the temperature dependence of D/D_T. Thus, polymers of decreasing M have a larger l value and therefore experience a higher mean temperature. Since D/D_T increases with temperature (11), the resulting increase in l with decreasing M is greater than that predicted without considering the temperature dependence.

METHODOLOGY

We use retention data reported in the literature (11, 13, 14) for four different molecular weight polystyrene standards evaluated by ThFFF over a range of cold-wall temperatures T_c in the carrier-liquid ethylbenzene. Values of the ratio D_T/D were calculated using Eq. (7) and the nonisoviscous corrections to Eq. (8), as outlined in Ref. 11; these data are summarized in Table 1. For each molecular weight, the temperature dependence of D_T/D was fit to the following equation:

$$\frac{D_T}{D} = \frac{e}{T + f} \tag{13}$$

If we approximate the thermal conductivity as constant between the hot and cold walls, then the temperature profile can be defined by the following linear equation:

$$T(x) = T_c + x(dT/dx) \tag{14}$$

Substituting Eqs. (13) and (14) into Eq. (3) yields

$$\frac{1}{c(x)}\frac{dc(x)}{dx} = -\left(\frac{e}{T_c + x(dT/dx) + f}\right)\frac{dT(x)}{dx} \tag{15}$$

Rearranging Eq. (15) and solving the resulting differential equation yields

$$c(x) = c_0 \exp\left[-e \ln\left(\frac{T_c + f + x(dT/dx)}{T_c + f}\right)\right] \tag{16}$$

For each molecular weight, the concentration profile given by Eq. (16), using a fixed cold-wall temperature, was inserted into Eq. (6) to obtain

TABLE 1
Values of D_T/D versus T for Polystyrenes in Ethylbenzene
(ΔT = 40 K; w = 0.0254 cm)

M	T	D_T/D	M	T	D_T/D
20,000	278	0.0996	97,000	308	0.2169
	278	0.1104		314	0.2213
	299	0.0883		339	0.1558
	313	0.0812		355	0.1482
	360	0.0589		371	0.1202
51,000	274	0.1869		388	0.1062
	275	0.1924		402	0.1032
	295	0.1502		418	0.0880
	315	0.1324		433	0.0818
	317	0.1413	160,000	271	0.4122
	342	0.1020		273	0.3890
	358	0.0877		292	0.3329
	374	0.0690		306	0.3023
	391	0.0634		338	0.2003
	405	0.0635		353	0.1943
	422	0.0509		369	0.1558
	437	0.0458		387	0.1450
97,000	272	0.3051		400	0.1335
	273	0.2989		416	0.1224
	279	0.2627		432	0.1125
	293	0.2355			

the corresponding $\bar{l}$ value. (Here, the bar over parameter l distinguishes the use of a temperature-dependent D_T/D in calculating its value.) Finally, selectivities were determined using the first equality in Eq. (11).

If we neglect the temperature dependence of D_T/D, Eq. (15) reverts to Eq. (3) and l values are calculated from Eq. (7). In these calculations the molecular weight dependence of D_T/D was accounted for, but the temperature effect is ignored by using D_T/D at 295 K.

RESULTS AND DISCUSSION

Figure 1 plots the values of D_T/D versus T for each molecular weight. The lines in Fig. 1 correspond to the fitted parameters in Eq. (13), which are summarized in Table 2. Table 3 compares $\bar{l}$ values obtained using the temperature dependence of D_T/D versus l values obtained when only the molecular weight dependence is considered. Plots of $\bar{l}$ and l versus M are plotted in Fig. 2. It is clear from these plots that the temperature depen-

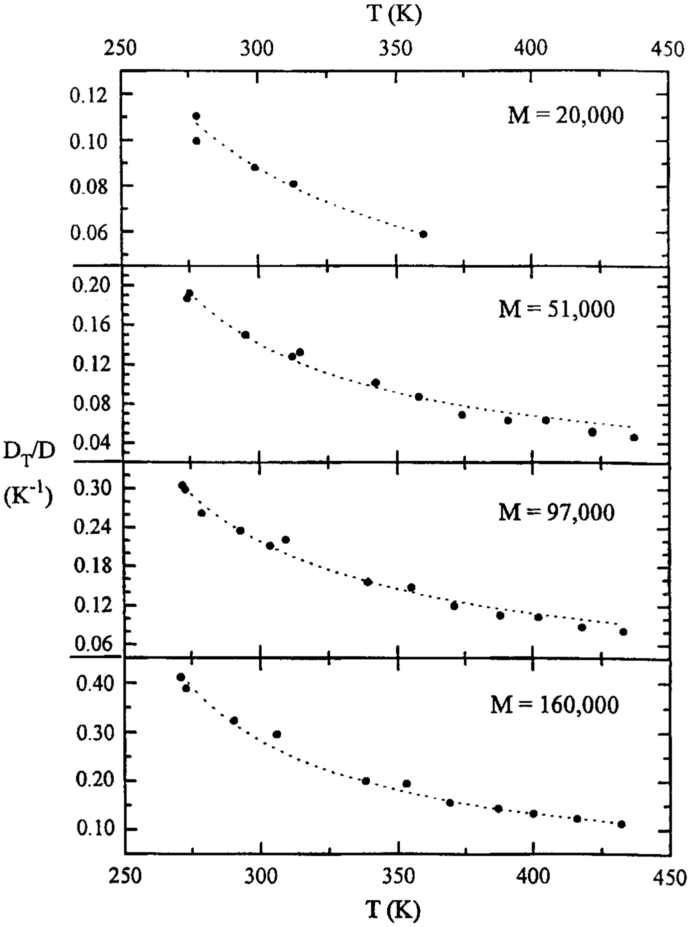

FIG. 1 D_T/D as a function of T for polystyrene in ethylbenzene. Points were obtained from data in Ref. 11; dashed lines are fitted functions of the form given in Eq. (13).

TABLE 2
Fitting Parameters for D_T/D versus T (Eq. 13)

M	*e*	*f*
20,000	11.398	−169.96
51,000	13.154	−206.79
97,000	21.738	−200.67
160,000	25.633	−210.53

TABLE 3
Calculated Mean Layer Thickness and Selectivity With ($\bar{l}$) and Without (l) a Temperature Dependence in D_T/D

M	$\bar{l}$ (μm)	l (μm)
20,000	84.5	69.7
51,000	50.3	42.6
97,000	30.3	27.6
160,000	22.4	21.6
Selectivity	0.646	0.574

dence of D_T/D increases the zone thickness considerably, and that the effect increases with decreasing molecular weight. As a result, different molecular weight components are spread out more across the channel, i.e., selectivity increases. The strong molecular weight dependence of the temperature effect is illustrated more directly in Fig. 3, which plots $l/\bar{l}$ as a function of M. The selectivities listed in Table 3 are slopes obtained by linear least squares on plots of the zone thickness versus ln M, as illus-

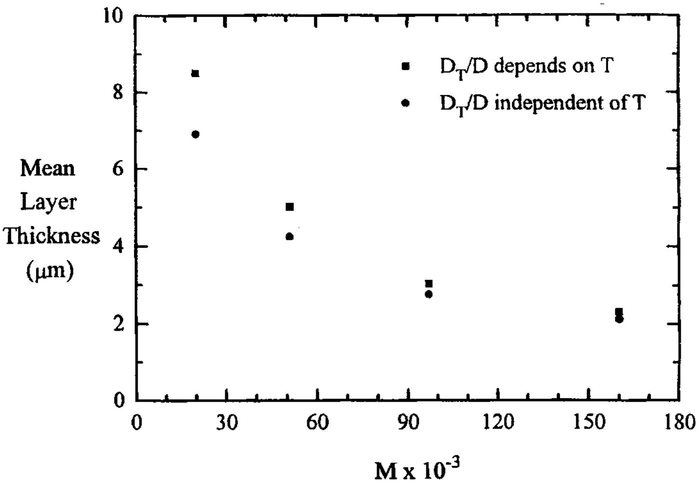

FIG. 2 Mean layer thickness as a function of molecular weight using Eq. (7) with and without allowing D_T/D to vary with temperature. In the latter case, T was held constant at 295 K (ΔT = 40 K; w = 0.0254 cm).

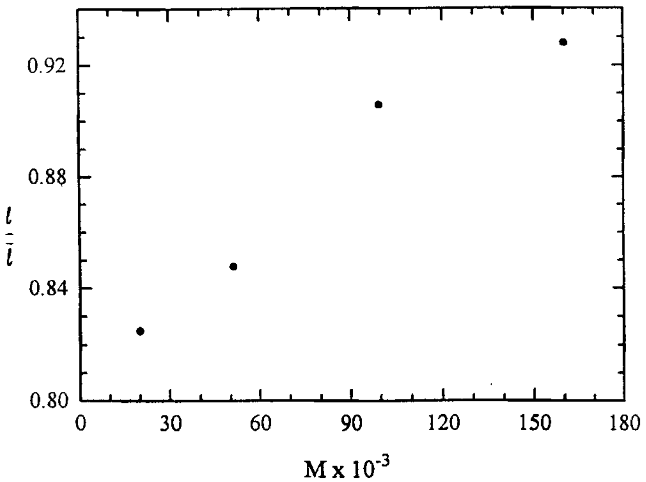

FIG. 3 Ratio $l/\bar{l}$ as a function of M (ΔT = 40 K; w = 0.0254 cm).

trated in Fig. 4. When the temperature effect is removed, the selectivity drops from 0.64$_6$ to 0.57$_4$. Thus, the temperature dependence of D_T/D significantly enhances the separation of polymers by mass in ThFFF. The s_l value of 0.57 is much closer to the b value of 0.55 previously reported

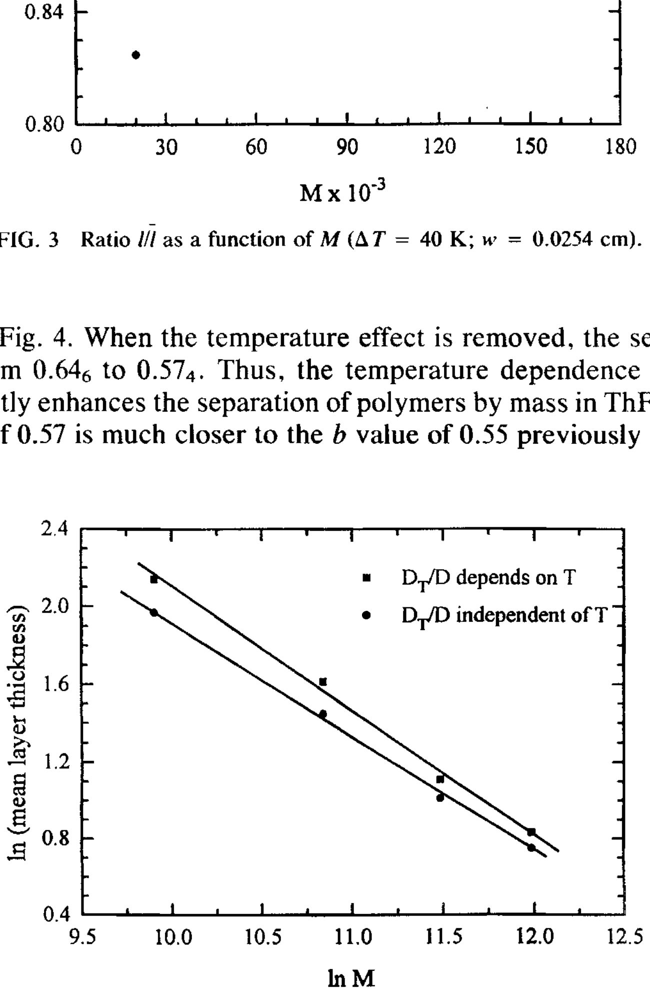

FIG. 4 Log-log plots of the mean layer thickness versus M. Selectivity is given by the slope of the lines, which were determined by linear least-squares.

(15) for polystyrene in ethylbenzene, and falls under the maximum value of 0.585 predicted by de Genne for a random-coil polymer dissolved in an ideal solvent.

While this work does not constitute proof that D_T is independent of M, it does demonstrates that mass selectivity in ThFFF is enhanced significantly beyond what is expected from polymer b-values. Furthermore, any dependence of D_T on degree of polymerization, if it exists, is very small. Although a precise statistical analysis of the uncertainty in reported selectivities is beyond the scope of this work, it is likely that such uncertainties are greater than the potential contribution of a D_T dependence on M.

The temperature T_l at the center of gravity is given by the following expression (5):

$$T_l = T_c + D/D_T \tag{17}$$

Thus, for a given polymer–solvent system, the temperature range across which a polymer component is distributed in the ThFFF channel is independent of the temperature gradient. As a result, the increase in selectivity that arises from the temperature dependence of D_T/D is independent of the difference in temperature ΔT between the hot and cold walls. On the other hand, the effect increases with the temperature range dT over which a calibration curve is obtained. However, this does not mean that calibration curves, which are typically plotted as ln D/D_T versus ln M, will necessarily be curved. If, in fact, the temperature dependence of D/D_T is exponential, as suggested by Brimhall et al. (11), then selectivity will be independent of dT as well as ΔT, and linear calibration curves can be expected.

ACKNOWLEDGMENTS

This work was funded by Idaho EPSCoR and Grant OSR9350539 from the National Science Foundation.

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Received by editor July 31, 1995