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Interpretation of thermal field-flow fractionation experiments in a tilted channel

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Abstract

Ryoo et al. [J. Kor. Chem. Soc., 39 (1995) 848] observed that the retention times of polymers in a tilted thermal field-flow fractionation channel significantly depend on the tilting angle, θ . Their results are quantitatively interpreted in the present study. It is found that the force directly exerted by the gravitational field on the macromolecules is much too small to account for the deviations observed. A reasonably good agreement is found between the experimental data obtained by Ryoo et al. and the retention times predicted by means of a model taking into account the free convection flow induced by the temperature dependence of carrier liquid density (thermogravitational effect). The measurement of the retention time at various θ , keeping flow and temperature differential constant, is suggested as a convenient method for determination of the sign of the Soret coefficient of macromolecular or colloidal species. © 1997 Elsevier Science B.V.

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1. Introduction

Thermal field-flow fractionation is a member of the field-flow fractionation (FFF) family of separation methods which are applicable to a wide variety of supramolecular species [1]. In FFF, the components of a sample are differentially retained according to their interaction with an external force field (or cross-flow) applied perpendicularly to the direction of the flow in a ribbon-like channel. In thermal FFF, the field applied is a temperature gradient, which allows the separation of various polymeric samples [2–4]. Most generally, the ther-

mal FFF channel is horizontal and the temperature gradient is vertical. In order to avoid possible Rayleigh–Bénard flow recirculations, associated with the unstable stratification of liquid layers of variable density, the hot and cold plates are, respectively, the top and bottom plates. The retention times of the sample components are adjusted mainly by means of the temperature difference between the plates, ΔT , and the flow-rate of carrier liquid.

In recent experiments, Ryoo et al. [5] observed that, for a constant carrier flow-rate and constant ΔT , the retention time of polystyrene and polymethylmethacrylate samples in tetrahydrofuran (THF) can be significantly modified by tilting the channel and that, for a given polymer, the absolute value of the

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retention time difference between the tilted and horizontal channel configurations increases when the angle, θ , between the main channel axis (flow axis) with the horizontal plane increases. Furthermore, they found that, for all injected samples, the retention times increase with increasing θ for upward carrier flow, and decrease with increasing θ for downward flow. This was attributed to a gravitational effect. The present study intends to provide a quantitative interpretation of the phenomena observed by Ryoo et al. [5].

2. Theory

2.1. Gravitational force exerted on a polymer molecule

The buoyancy-corrected net force, F_g , exerted by the Earth's gravitational field on a polymer molecule is given by:

$$F_g = \frac{M}{N_{Av}} g \frac{\Delta\rho}{\rho_p} \quad (1)$$

where M is the molar mass, N_{Av} , the Avogadro number, g , the gravitational acceleration, ρ_p , the density of the polymer, and $\Delta\rho$, the density difference between the polymer and the solvent. This force may contribute to the retention time in thermal FFF in two ways. First, its component along the applied thermal gradient will modify the degree of compression of the polymer cloud near the accumulation wall, and, second, its component along the flow direction will make the macromolecules move faster or slower than the unperturbed carrier at the same position, depending on the flow direction and on the sign of $\Delta\rho$.

As for the first effect, the component of this force along the thermal gradient, i.e., $F_g \cos \theta$, where θ is the angle between the channel axis and the horizontal in a vertical plane, will combine to the thermophoretic force to move the polymer molecules near the accumulation wall. The total force exerted on a macromolecule is:

$$F_{tot} = F_g \cos \theta \pm F_{th} \quad (2)$$

It is largest when $\theta=0$, i.e., when the channel is horizontally oriented. The sign depends on the relative directions of the two forces along the thermal gradient. The total force is related to the basic FFF retention parameter, λ , in the Brownian retention mode by:

$$\lambda = \frac{kT}{F_{tot} w} \quad (3)$$

where k is the Boltzmann constant, T the absolute temperature, and w the channel thickness. From Eqs. (1)–(3), one gets the relative contribution of the gravitational force (in the horizontal channel) to the total force:

$$\frac{F_g}{F_{tot}} = \lambda \cdot \frac{Mgw}{\mathcal{R}T} \cdot \frac{\Delta\rho}{\rho_p} \quad (4)$$

where \mathcal{R} is the ideal gas constant. It is seen that this relative contribution is the largest when the retention parameter is the largest. Let us take 0.2 as the maximum practical value for λ (larger values of λ would lead to peaks hardly distinguishable from the void peak in FFF). A numerical calculation, for $M=300\,000 \text{ g mol}^{-1}$, $w=127 \text{ }\mu\text{m}$, $g=981 \text{ cm s}^{-2}$, $T=300 \text{ K}$ and $\Delta\rho/\rho_p=0.25$, gives a relative contribution of the gravitational force to the total force equal to about $7 \cdot 10^{-4}\%$. This contribution is therefore totally negligible and its change with θ is unmeasurable.

The axial velocity contribution of the force, $v_{g,ax}$, is equal to $F_g \sin \theta / f$. f , the friction factor, is related to the diffusion coefficient, which itself depends on the molar mass as A/M^b , where A and b are constants for a given polymer–solvent system at a given temperature. One then gets, in combination with Eq. (1), when the channel is vertically oriented ($\sin \theta=1$):

$$v_{g,ax} = \frac{AM^{1-b} g}{\mathcal{R}T} \cdot \frac{\Delta\rho}{\rho_p} \quad (5)$$

Using values given above and characteristic values of A and b for the polystyrene/ethylbenzene system [6], one gets $7 \cdot 10^{-10} \text{ cm s}^{-1}$, i.e., $0.6 \text{ }\mu\text{m}$ per day. Again, this velocity shift is completely negligible.

It thus appears that the force directly exerted by

the gravitational Earth field on the polymer molecules cannot give measurable effect on retention, whatever the orientation of the channel and cannot explain the drastic variations of polymer retention times with the angle θ observed by Ryoo et al. [5] in their experiments.

2.2. Thermogravitational effect

Thermal FFF experiments in a vertical channel have been conducted in the past. The retention of polystyrene standard samples was shown to be significantly different from that observed in the horizontal configuration [7]. The direction of the retention change was shown to depend on the flow direction (upward or downward). These observations were quantitatively described as due to the thermogravitational effect. Thermogravitational FFF experiments at various flow-rates allow to determine the sign of the Soret coefficient, i.e., to indicate whether, in a thermal gradient, the macromolecules migrate toward the hot or cold wall [8]. The influence of the thermogravitational effect on thermal FFF retention times in a tilted channel is evaluated below.

The thermogravitational effect arises from the temperature dependence of the liquid density in a horizontal temperature gradient. Then, the lighter liquid near the hot region tends to move upward while the heavier liquid near the cold wall flows downward. This free convection flow arises from the fact that the hydrostatic pressure gradient is not constant in a cross-section. The resulting free convection profile has been derived from the Navier–Stokes equation, in laminar conditions, under the assumption of a constant viscosity, of a linear temperature gradient and of a linear dependence of the liquid density on temperature (see, for instance, Ref. [9]). In the case of a tilted channel, the hydrostatic pressure gradient along the channel axis is equal to $\rho g \sin \theta$, where ρ is the liquid density, which depends on the distance x from the cold wall. Then, the free convection velocity profile obtained in a vertical channel can be used to get the free convection profile in a tilted channel by replacing the gravitational acceleration, g , by its component along the channel axis, $g \sin \theta$. Thus, in the free convection situation, when the viscous forces are just balanced

by the buoyancy forces, the resulting profile in a long channel (i.e., a channel of length L much larger than w , as is the case in thermal FFF), far from either inlet or outlet, depends only on x and is given by [7,9]:

$$v_{\text{free}} = \frac{\rho_m \gamma g \sin \theta w^2 \Delta T}{12 \eta_m} \times \left[\left(\frac{x}{w} \right) - 3 \left(\frac{x}{w} \right)^2 + 2 \left(\frac{x}{w} \right)^3 \right] \quad (6)$$

where γ is the thermal expansion coefficient of the liquid (i.e., relative rate of variation of volume with temperature, assumed constant within the temperature range in the channel), ΔT the temperature drop between the hot and cold plates, ρ_m and η_m , respectively, the liquid density and viscosity at the average temperature in the channel.

In a classical (horizontal) thermal FFF channel, the flow velocity profile, $v_{\text{forced}}(x)$, is given by [10]:

$$v_{\text{forced}}(x) = 6 \langle v \rangle \times \left[(1 + \nu_{\text{hor}}) \left(\frac{x}{w} \right) - (1 + 3\nu_{\text{hor}}) \left(\frac{x}{w} \right)^2 + 2\nu_{\text{hor}} \left(\frac{x}{w} \right)^3 \right] \quad (7)$$

where x is the distance from the accumulation wall, w the channel thickness, $\langle v \rangle$ the cross-sectional average flow velocity and ν_{hor} , a flow distortion parameter which accounts for the deviation from the parabolic Poiseuille profile due to the temperature dependence of the carrier liquid viscosity. From Eq. (7), it appears that $1 + \nu_{\text{hor}}$ is the ratio of the actual velocity profile near the cold wall in the thermal FFF channel to that of a hypothetical parabolic profile with the same average velocity, $\langle v \rangle$. (One notes that, in order to solve the Navier–Stokes equation for the free flow, the viscosity dependence of temperature was not taken into account because it is supposed to bring only a second-order correction compared to that of the temperature dependence of the density which gives rise to this free flow).

To a first approximation, the total flow profile, v_{tot} , obtained in a tilted channel is the sum of the free profile in absence of forced flow and of the forced flow obtained without free flow in a horizontal configuration. From Eqs. (6) and (7), one gets:

$$\begin{aligned} \frac{v_{\text{tot}}(x)}{\langle v \rangle} &= \frac{v_{\text{forced}}(x) + v_{\text{free}}(x)}{\langle v \rangle} \\ &= 6 \left[(1 + \nu_{\text{tot}}) \left(\frac{x}{w} \right) - (1 + 3\nu_{\text{tot}}) \left(\frac{x}{w} \right)^2 \right. \\ &\quad \left. + 2\nu_{\text{tot}} \left(\frac{x}{w} \right)^3 \right] \end{aligned} \quad (8)$$

with:

$$\begin{aligned} \nu_{\text{tot}} &= \nu_{\text{hor}} + \delta \cdot \frac{\rho_m \gamma g \sin \theta w^2 \Delta T}{72 \eta_m \langle v \rangle} \\ &= \nu_{\text{hor}} + \delta \nu_{\text{vert}} \sin \theta \end{aligned} \quad (9)$$

and:

$$\nu_{\text{vert}} = \frac{\rho_m \gamma g w^2 \Delta T}{72 \eta_m \langle v \rangle} \quad (10)$$

where $x=0$ at the cold wall, $\delta = -1$ for upward flow and $\delta = +1$ for downward flow (note that γ is generally positive, $\langle v \rangle$ is chosen positive, and, whatever the flow direction, θ is positive). ν_{vert} represents the contribution of the free convection profile to the flow distortion parameter when the channel is vertically oriented ($\sin \theta = 1$).

The retention ratio, for the flow profile of Eq. (8) and an exponential transversal concentration for polymers accumulating at the cold wall ($x=0$), is given by [7]:

$$R = R_p + 6\lambda(1 - R_p)\nu_{\text{tot}} \quad (11)$$

where R_p , the retention ratio which would be obtained if the velocity profile was parabolic, is given by the classical retention equation:

$$R_p = 6\lambda \left[\coth\left(\frac{1}{2\lambda}\right) - 2\lambda \right] \quad (12)$$

Since it was shown above that the force directly exerted on the macromolecules by the gravitational field is totally negligible, λ and R_p are fixed and do not depend on the channel orientation when the temperature drop between the plates and the cold wall temperature are fixed. Let R_0 be the retention ratio in the horizontal configuration:

$$R_0 = R_p + 6\lambda(1 - R_p)\nu_{\text{hor}} \quad (13)$$

From Eqs. (9), (11), (13), the retention time,

$t_R(\theta)$, of a given species in the tilted channel is given by:

$$\begin{aligned} t_R(\theta) &= \frac{t_0}{R} = \frac{t_0}{R_0 + 6\lambda(1 - R_p)\delta\nu_{\text{vert}}\sin\theta} \\ &= \frac{t_R(0)}{1 + 6\lambda\left(\frac{1 - R_p}{R_0}\right)\delta\nu_{\text{vert}}\sin\theta} \end{aligned} \quad (14a)$$

or:

$$t_R(\theta) = \frac{t_R(0)}{1 + \left(1 - \frac{R_p}{R_0}\right)\delta \cdot \frac{\nu_{\text{vert}}}{\nu_{\text{hor}}} \cdot \sin\theta} \quad (14b)$$

or, still:

$$\frac{t_R(0)}{t_R(\theta)} = 1 + S \sin \theta = 1 + \delta|S| \sin \theta \quad (14c)$$

with S given by

$$S = \delta|S| \quad (15a)$$

and

$$|S| = 6\lambda \left(\frac{1 - R_p}{R_0} \right) \nu_{\text{vert}} = \left(1 - \frac{R_p}{R_0} \right) \cdot \frac{\nu_{\text{vert}}}{\nu_{\text{hor}}} \quad (15b)$$

where t_0 is the void time required to flush the channel at the selected flow-rate, and $t_R(0)$ the retention time of that species in a horizontal channel under identical temperature and flow-rate conditions. When $S \sin \theta$ is quite smaller than unity, Eq. (14c) can be approximated by:

$$t_R(\theta) = t_R(0)[1 - S \sin \theta] \quad (16)$$

From Eq. (14a), one gets the relative variation in retention time which should be observed when going from the horizontal to the vertical orientation of the channel:

$$\frac{t_R(90) - t_R(0)}{t_R(0)} = \frac{1}{1 + S} - 1 \quad (17)$$

where $t_R(90)$ is the analyte retention time in the vertical channel. The retention time difference, $\Delta t_R(\theta)$, between two analytes, in the tilted configuration, becomes:

$$\Delta t_R(\theta) = t_{R,2}(\theta) - t_{R,1}(\theta) = \frac{t_0(R_{0,1} - R_{0,2})}{R_1 R_2} \times \left\{ 1 + 6\delta \nu_{\text{vert}} \sin \theta \cdot \frac{[\lambda_1(1 - R_{p,1}) - \lambda_2(1 - R_{p,2})]}{(R_{0,1} - R_{0,2})} \right\} \quad (18)$$

where subscripts 1 and 2 refer to analytes 1 and 2. It can be shown that, when analyte 2 is more retained than analyte 1, i.e., when λ_1 is greater than λ_2 , the term in parenthesis in the numerator of Eq. (18) is positive, as are the denominators. However, as R_1 and R_2 also depend on θ , the direction of variation of $\Delta t_R(\theta)$ with θ is not easy to determine from Eq. (18). Nevertheless, if limiting expressions of R in the high retention domain are taken [$R = 6(1 + \nu_{\text{tot}})\lambda$], Eq. (18) becomes:

$$\Delta t_R(\theta) = \frac{\Delta t_R(0)}{1 + \delta \frac{\nu_{\text{vert}}}{1 + \nu_{\text{hor}}} \cdot \sin \theta} \quad (19)$$

3. Experimental

The thermal FFF channel used by Ryoo et al. [5] was similar to those used by previous thermal FFF studies. The two plates were in copper, the hot (top) one was heated by electrical heaters while the cold

(bottom) one was cooled by a flow of coolant. The channel, of dimensions 0.127 mm \times 2 cm \times 54.3 cm (tip-to-tip length), was cut in a polyester spacer. The channel-flow arrangement is schematically depicted in Fig. 1. Tetrahydrofuran was used as carrier liquid and polymer solvent. Samples were polystyrene and polymethacrylate standards of nominal polydispersity index of about 1.04.

4. Discussion

The residence time of an unretained solute is simply given as the channel void volume divided by the flow-rate. As the free convection part of the total flow in Eq. (8) does not contribute to the flow-rate, this void time should not depend on the orientation of the channel. This is observed in Figure 5 of Ryoo et al. [5] where the residence time of ethylbenzene, an analyte with a very low molar mass to be significantly affected by the thermal gradient, appears to be constant whatever θ . This is confirmed by the fractograms of Figure 14 of Ryoo et al. [5] where the void peak appears at the same elution time whatever the orientation of the channel and flow direction, under constant flow-rate. However, a slight shift in the curve of residence time of ethylbenzene vs. $\sin \theta$ for upward flow experiments is apparent in Figure 9 of Ryoo et al. [5]. One believes this is due to a slight variation of the flow-rate from one run to another or within a given run. It may indeed not be easy to maintain constant the flow-rate at quite a low value over a period of time of about 2 h.

The retention times of two polystyrene (PS) samples and of two polymethylmethacrylate (PMMA) samples are reported versus $\sin \theta$ for both downward and upward flow experiments in Figures 6 (PS-downward), 8 (PMMA-downward), 10 (PS-upward) and 11 (PMMA-upward) of Ryoo et al. [5], while the retention time differences between the two PS samples and between the two PMMA samples are reported in Figures 12 (downward flow) and 13 (upward flow) of Ryoo et al. [5]. For each sample-flow arrangement, the data appear to reasonably lie on a straight line with positive slope for upward flow and negative slope for downward flow. Eqs. (14a–c), (15a,b), (16)–(19) can be used to analyze the

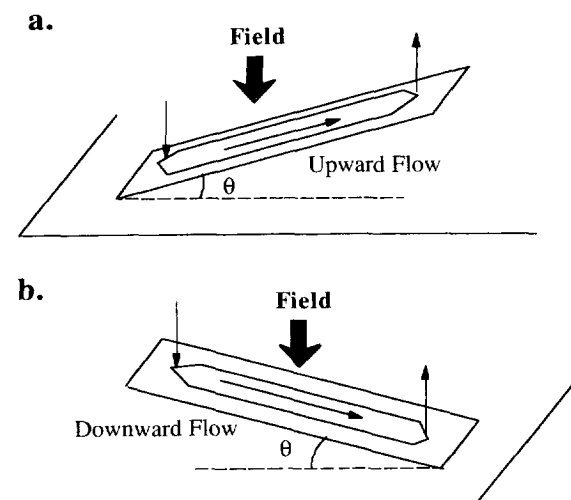


Fig. 1. Schematic diagram of the tilted channel in the upward (a) and downward (b) flow configurations.

experimental data reported in these Ryoo et al. Figures [5].

As R_p is less than 1, Eq. (14a) shows that, when the flow-rate as well as the cold and hot wall temperatures are kept constant, i.e., when λ , ν_{hor} and ν_{vert} are constant, hence when $|S|$ is constant, the retention time of a polymer sample accumulating at the cold wall should be a hyperbolic function of $\sin \theta$. According to Eq. (16), this function can, for relatively small S values, be approximated by a straight line, which increases with $\sin \theta$, i.e., from horizontal to vertical channel configuration, for upward flow ($\delta = -1$), and decreases for downward flow ($\delta = +1$). This is in qualitative agreement with the experimental observations of Ryoo et al. [5]. Similarly, although the R values of the two polystyrene (PS) and two PMMA analytes do not correspond to the high retention domain (see below), it is found that the direction of variation of Δt_R with $\sin \theta$ for these samples in Figures 12 and 13 of Ryoo et al. [5] is in agreement with that predicted from Eq. (19).

One can check the consistency between the experimental data obtained for upward and downward flow. As temperature and flow conditions are the same in the two kinds of experiments, the only difference in the relative change of t_R of a given analyte from horizontal to vertical configurations in Eqs. (15a), (15b), (16) is in the sign of δ . Therefore, the same values of $|S|$ should be obtained from the determination of t_R in upward and downward flow. From data reported in Figures 6 and 10 of Ryoo et al. [5] for the polystyrene sample with molar mass of 156 000 (PS 156k), which gives relative t_R changes of -22.2% and $+37.3\%$ as the channel orientation changes from horizontal to vertical, one finds that $|S|$, computed, according to Eq. (14c), as $\delta\{t_R(0)/t_R(90)\} - 1$, is equal to 0.283 and 0.272 for downward and upward flow, respectively. In view of the limited precision of the determinations of retention times, this agreement is remarkable (only 4% difference) and strongly supports the validity of the present analysis based on the thermogravitational effect to explain the variations of retention with θ .

This consistency can be checked for all values of θ by plotting $t_R(0)/t_R(\theta)$ versus $\delta \sin \theta$ for both upward and downward flow when experiments are done in identical temperature and flow conditions. Such a plot is shown in Fig. 2 for the PS 156k

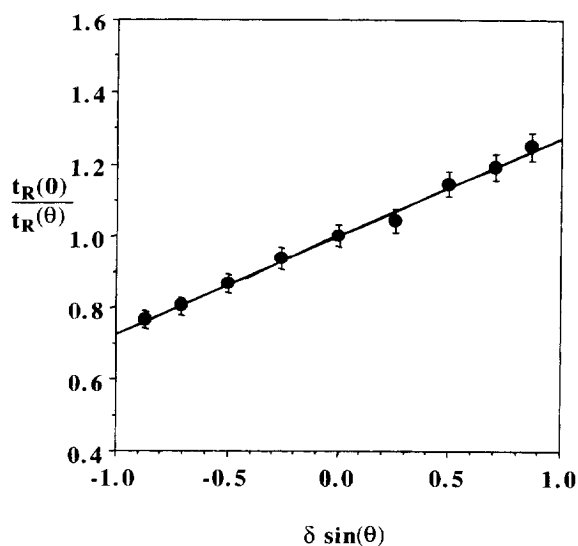


Fig. 2. Variations of $t_R(0)/t_R(\theta)$ vs. $\delta \sin \theta$, for the PS 156k sample injected alone. The negative (positive) $\delta \sin \theta$ data correspond to upward (downward) flow experiments. The error bars correspond to a 2% error on each t_R determination. The straight line is a least mean square linear regression fit to the data. $\Delta T = 43.5$ K, $T_c = 294$ K.

sample. Negative $\delta \sin \theta$ data correspond to upward flow and positive $\delta \sin \theta$ data to downward flow. According to Eq. (14c), all data points should lie on a single line of slope equal to $|S|$. It is seen all experimental points fit fairly well on a straight line, within experimental uncertainties, which confirms the consistency of the upward and downward data.

The comparison between the data of Ryoo et al. [5] and those generated by the above equations can be made more quantitative by comparing the experimental values of ν_{vert} ($\nu_{\text{vert,exp}}$) obtained by fitting experimental t_R data to Eq. (14a) with the value computed from Eq. (10). Every comparison of two retention time values for the same analyte, same flow and temperature conditions at two different θ angles can lead to an estimate of ν_{vert} . However, in order to get average values, one chooses to estimate ν_{vert} from the slope, S , of $t_R(0)/t_R(\theta)$ versus $\sin \theta$ plots, which allows one to take into account data obtained at various angles. Such plots are shown in Fig. 3, for the PS 156k sample, and Fig. 4, for the PMMA 330k sample (PMMA with molar mass of 330 000). They correspond to data reported by Ryoo et al. [5] in their Figures 6 (PS 156k, downward

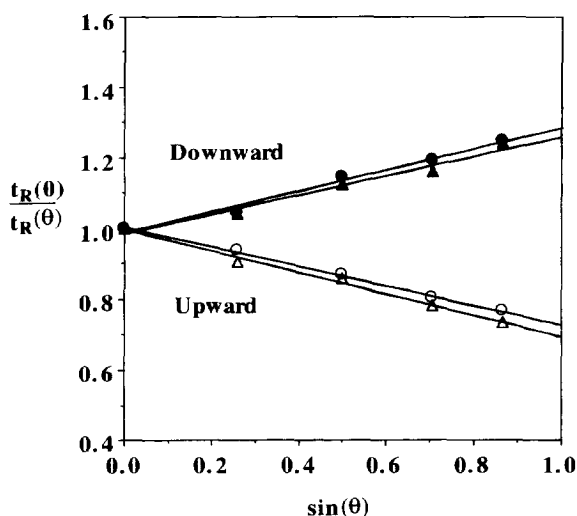


Fig. 3. Variations of $t_R(0)/t_R(\theta)$ vs. $\sin \theta$ for PS 156k. $\Delta T=43.5$ K, $T_c=294$ K. The regression lines are also plotted. (○) Sample injected alone, upward flow. (△) Sample injected together with PS 66k, upward flow. (●) Sample injected alone, downward flow. (▲) Sample injected together with PS 66k, downward flow.

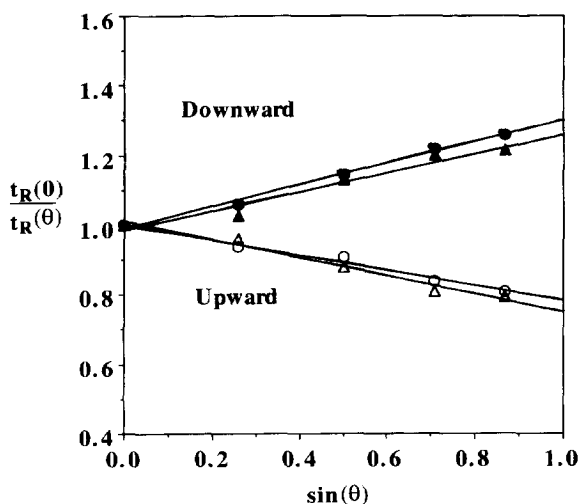


Fig. 4. Variations of $t_R(0)/t_R(\theta)$ vs. $\sin \theta$ for PMMA 330k. Upward flow: $\Delta T=41$ K, $T_c=297.15$ K. Downward flow: $\Delta T=42$ K, $T_c=296.15$ K. The regression lines are also plotted. (○) Sample injected alone, upward flow. (△) Sample injected together with PMMA 63k, upward flow. (●) Sample injected alone, downward flow. (▲) Sample injected together with PMMA 63k, downward flow.

flow), 8 (PMMA 330k, downward flow), 10 (PS 156k, upward flow) and 11 (PMMA 330k, upward flow). One chooses to compare t_R data in the horizontal and tilted conditions for the most retained compounds as they are the least affected by interference with the void peak and are expected to lead to more accurate retention values. In Figs. 3 and 4, curves with positive and negative slopes correspond to downward and upward flow, respectively. For each sample and each flow direction, two sets of data are shown. They correspond to retention data obtained when the samples were injected separately or when mixtures of the sample and another one of lower molar mass were injected. The regression lines are also plotted in Figs. 3 and 4 for each data set. These linear regressions are seen to provide good fit to the data as the correlation coefficients are in all cases larger than 0.97. According to Eq. (14a), ν_{vert} is computed as:

$$\nu_{\text{vert,exp}} = \frac{\nu_{\text{hor}}}{|S| \left(1 - \frac{R_p}{R_0}\right)} \quad (20)$$

The $\nu_{\text{vert,exp}}$ values obtained from this equation are reported in Table 1. The value of ν_{hor} can be computed from ΔT and T_c , the cold wall temperature, for a given solvent, according to a previously developed procedure [11]. ν_{hor} is found equal to -0.131 for conditions of the PS 156k downward and upward experiments, -0.125 for the PMMA 330k downward experiments and -0.122 for the PMMA 330k upward experiments. The slight difference between the ν_{hor} values for these three sets of experiments arises mostly from a slight change in ΔT . R_0 is determined as $t_0/t_R(0)$. λ is then obtained from R_0 and ν_{hor} by means of the combination of Eqs. (11) and (12) and R_p is calculated using Eq. (12). The S values have been obtained from linear regression of the data in Figs. 3 and 4 and are reported in Table 1 together with the intermediate parameters. For each sample-flow direction combination, the top and bottom lines in Table 1 correspond to the separate injection and mixture injection, respectively. The average $\nu_{\text{vert,exp}}$ values for the PS and PMMA-downward and PMMA-upward experiments are respectively, equal to $0.465 \pm 6\%$, $0.359 \pm 6\%$ and $0.296 \pm 15\%$.

Table 1
Values of $\nu_{\text{vert,exp}}$ obtained from experimental retention data using Eq. (20)

Sample/ flow direction	δ	ν_{hor}	t_0 (min)	$t_R(0)$ (min)	R_0	λ	R_p	S	$\nu_{\text{vert,exp}}$
PS 156k/ downward	+1	−0.131	29.7	56.1	0.529	0.128	0.572	+0.296	0.476
				55.2	0.538	0.131	0.581	+0.272	0.443
PS 156k/ upward	−1	−0.131	29.7	56.1	0.529	0.128	0.572	−0.275	0.442
				55.2	0.538	0.131	0.581	−0.300	0.499
PMMA 330k/ downward	+1	−0.125	26.6	82.9	0.321	0.0685	0.355	+0.310	0.375
				76.9	0.346	0.0747	0.381	+0.274	0.344
PMMA 330k/ upward	−1	−0.122	26.6	82.7	0.322	0.0683	0.354	−0.219	0.265
				75.9	0.351	0.0755	0.385	−0.260	0.327

For each sample-flow direction arrangement, the upper data correspond to the polymer injected alone in the channel while the lower data are obtained from injection of a mixture of two polymers of the same chemical nature but of different molar masses giving two partially resolved peaks.

These values can be compared with those, $\nu_{\text{vert,est}}$, estimated from the definition of ν_{vert} in Eq. (10). The average flow velocity is determined from the flow-rate, Q , as $\langle v \rangle = Q/bw$, where b is the channel breadth (2 cm) and w the channel thickness (127 μm). The viscosity η_m , of tetrahydrofuran at the average temperature, $T_m (= T_c + \Delta T/2)$, where T_c is the cold wall temperature), in the channel can be calculated from the Andrade equation (with $\eta = 0.575$ cP at $T = 293$ K and $B = 923.21$ K, see Ref. [11]). The determinations of the solvent density and thermal expansion coefficient have been made from computation of the solvent molar volumes at various temperatures, according to the Hankinson–Brobst–Thomson method suggested by Reid et al. [12]. The values of the parameters involved in Eq. (10) are given in Table 2 together with the resulting values of $\nu_{\text{vert,est}}$.

It thus appears that, in average, the estimated values exceed the experimental ones by 37%, 43% and 69% for the PS, PMMA-downward and PMMA-upward experiments, respectively. Although these differences are significant and exceed the experimental uncertainties, one notes that the $\nu_{\text{vert,exp}}$ and $\nu_{\text{vert,est}}$ are of the same order of magnitude. This gives a further indication that the analysis presented in Section 2 is essentially correct. The fact that $\nu_{\text{vert,est}}$ exceeds $\nu_{\text{vert,exp}}$ shows that the thermogravitational effect can fully explain the variations of retention times observed by Ryoo et al. [5] in their experiments in the tilted thermal FFF channel. In order to explain the difference between these values, one may invoke a number of possibilities. First, one notes that Eq. (6) for ν_{free} is an approximation since it does not take into account the influence of temperature dependence of viscosity on the free

Table 2
Values of the parameters involved in Eq. (10) and of the resulting $\nu_{\text{vert,est}}$

Sample/ flow direction	$\langle v \rangle$ (cm s^{-1})	ΔT (K)	T_c (K)	η_m (cP)	γ (K^{-1})	ρ_m (g cm^{-3})	$\nu_{\text{vert,est}}$
PS 156k/ downward and upward	0.0381	43.5	294	0.457	$1.34 \cdot 10^{-3}$	0.862	0.638
PMMA 330k/ upward	0.0459	41	297.15	0.450	$1.34 \cdot 10^{-3}$	0.860	0.501
PMMA 330k/ downward	0.0459	42	296.15	0.452	$1.34 \cdot 10^{-3}$	0.861	0.512

convection profile. As noted above, this influence was thought to be only a second-order effect, however, because of the relatively large value of ν_{vert} , this influence may not be negligible. Second, the data used for the parameters involved in the expression of $\nu_{\text{vert,est}}$ may also be in error. Especially, one notes that $\nu_{\text{vert,est}}$ is quite sensitive to a small error in the channel thickness. Indeed, assuming a correctly measured flow-rate, it is seen that a 5% error in w leads to a 16% error in $\nu_{\text{vert,est}}$. Besides, as noted earlier in this section, the actual flow-rate may somewhat differ from the stated value. In addition, the values of ρ_m , η_m and γ may be somewhat erroneous. It is not infrequent that methods of estimation of, for instance, viscosity lead to errors exceeding 10%. Also, some error may arise from the fact that the temperature at which the viscosity has to be computed may differ from the centerline temperature as the relative rate of variation of viscosity with temperature is about 1% per degree K.

The experiments of Ryoo et al. [5] resemble those of Giddings et al. [7] in that both studies report a change in retention (time or ratio) vs. $\nu_{\text{vert}} \sin \theta$. In one case [7], variations of ν_{vert} at constant $\theta = 90^\circ$ are induced by changes in $1/\langle v \rangle$, while, in the other case [5], $\sin \theta$ is varied at constant $\langle v \rangle$. It is interesting to note that the vertical ThFFF channel experiments of Giddings et al. [7] also led to a $\nu_{\text{vert,est}}$ value largely exceeding (by 93%) the experimental one. This similar overestimation of ν_{vert} suggests that a systematic error occurs in the assumptions leading to the expression of the free convection velocity profile in Eq. (6). This error might be linked to the neglect of the temperature-dependence of viscosity in this equation.

It has been shown that increasing ν_{vert} with upward flow allows one to improve the selectivity and, to a lesser extent, the resolution, of modestly retained compounds [7]. This is, however, obtained at the expense of a significant increase in analysis time. Such a resolution improvement is also apparent in the fractograms of the PS samples in upward flow reported in Figure 14 of Ryoo et al. [5]. Besides, the determination of retention at various flow-rates in a vertical channel was shown to be a nice method of determination of the sign of the Soret coefficient of macromolecular (and, more generally, of colloidal) species, i.e., of the direction of migration of the

analytes in the thermal gradient (toward hot or cold plate), which cannot be obtained from experiments in a horizontal channel [8]. Indeed, if the analyte accumulates at the cold plate, for a given flow-rate, the velocity near the cold wall is smaller – and the retention time larger – in a vertical channel for upward flow than it would be in a horizontal channel because of the free convection part of the flow is in direction opposite to the forced flow near this wall. The opposite is true if the analyte accumulates at the hot wall or for downward flow. The retardation effect is more pronounced at low than at high flow-rate because the relative contribution of the free convection flow is more important. Such experiments are important for the physicochemical investigation of the thermal diffusion behavior of polymers because of the lack of a satisfying theory for predicting the sign of the Soret coefficient.

Similarly, the Ryoo et al. [5] experiments prove to be an alternative method of determination of the sign of the Soret coefficient. Indeed, as the migration velocity of both PS and PMMA samples in THF is retarded for upward flow when θ increases, it can be deduced that the samples are accumulating at the wall near which the free convection flow is in the opposite direction to the forced flow, i.e., in the downward direction. Hence, the samples are accumulating at the cold wall. The same conclusion is reached from downward flow experiments. Previous experiments have shown that PS and PMMA are migrating toward the cold regions in a thermal gradient [7,8]. However, these experiments were performed in other solvents (ethylbenzene, dimethylformamide). Therefore, the Ryoo et al. [5] experiments indicate that these polymers behave in THF as in these other solvents.

5. Symbols

A	prefactor of the power law of diffusion coefficient vs. molar mass
b	exponent in the power law of diffusion coefficient vs. the reciprocal of molar mass
f	friction factor of a polymer molecule
F_g	buoyancy-corrected net gravitational force exerted on a polymer molecule

F_{th}	thermophoretic force exerted on a polymer molecule	θ (positive)	angle between channel axis (i.e., flow axis) and the horizontal in a vertical plane
F_{tot}	total force exerted on a polymer molecule	λ	FFF retention parameter
g	gravitational acceleration	ν_{hor}	flow distortion parameter in the horizontal configuration
k	Boltzmann constant	ν_{tot}	total flow distortion parameter
M	molar mass	ν_{vert}	contribution of the free convection flow to the total flow distortion parameter
N_{Av}	Avogadro number	$\nu_{\text{vert,exp}}$	experimentally determined value of ν_{vert} (Eq. (20))
\mathcal{R}	ideal gas constant	$\nu_{\text{vert,est}}$	estimated value of ν_{vert} (Eq. (10))
R	retention ratio in tilted thermal FFF channel	ρ_{m}	solvent density at average temperature in the channel
R_0	retention ratio in the horizontal thermal FFF channel	ρ_{p}	density of the polymer
R_{p}	retention ratio for a hypothetical parabolic flow profile	$\Delta\rho$	density difference between polymer and solvent
S	parameter defined by Eq. (15a)		
t_0	void time		
$t_{\text{R}}(0)$	retention time in horizontal channel		
$t_{\text{R}}(\theta)$	retention time in tilted channel		
$t_{\text{R}}(90)$	retention time in vertical channel		
$\Delta t_{\text{R}}(\theta)$	difference in retention times of two analytes in the tilted channel		
T	absolute temperature		
ΔT (positive)	temperature difference between the two channel plates		
$v_{\text{g,ax}}$	contribution of gravitational force to the axial velocity of a polymer molecule		
v_{forced}	forced flow velocity in the horizontal configuration		
v_{free}	free convection flow velocity arising from thermogravitational effect		
v_{tot}	total (forced plus free) flow velocity in the tilted configuration		
$\langle v \rangle$	average flow velocity		
w	channel thickness		
x	distance from the cold (accumulation) wall		
γ	thermal expansion coefficient		
δ	flow direction indicator (= -1 for upward flow; = +1 for downward flow)		
η_{m}	solvent viscosity at average temperature in the channel		

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