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ABSTRACT

In this work equations are presented to describe solute concentration profiles in thermal field-flow fractionation that account for the effect of the temperature drop across the solute zone on the thermal and ordinary diffusion coefficients. The influence of this effect, together with the effects of the temperature dependence of the solvent viscosity and solvent thermal conductivity, on the conversion of retention data into thermal diffusion data were studied. The systematic error made when the ratio of the thermal and ordinary diffusion coefficient (α/T) is assumed to be constant can be considerable and is larger for systems with low retention (e.g., for low molecular weight or small thermal diffusion). For the two systems studied (polystyrene in THF and in ethylbenzene), it was found that the temperature dependence of the solvent viscosity is of much greater importance than the temperature dependence of the solvent thermal conductivity. When all three parameters are considered to be independent of the temperature, the results are still quite acceptable. This is due to the fact that the effect of the temperature dependence of the solvent viscosity is counteracted by the combined effects of the temperature dependence of the solvent thermal conductivity and of α/T.

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INTRODUCTION

Field-flow fractionation (FFF) is a relatively new separation method introduced by Giddings in 1966 (1). This technique is especially suited to the analysis and characterization of macromolecules. Contrary to chromatographic separation methods, no stationary phase is used in FFF. Retention and separation are caused by the action of an external field perpendicular to the direction of the laminar flow of a carrier liquid through the open channel. Thermal field-flow fractionation (ThFFF) is a variety of FFF in which a temperature gradient is used as the field. In ThFFF, retention is determined by the ratio of the thermal to the ordinary diffusion coefficient. The ratio of these parameters is also expressed as α/T, where α is the Soret coefficient and T is the temperature.

The phenomenon of thermal diffusion has been known for over a century. The use of this transport process for the fractionation of macromolecules was first reported by Debye and Bueche (2) in 1948. A number of theories, which vary widely in conceptual basis, have been proposed to explain the phenomenon of thermal diffusion in liquids and to link the Soret coefficient to physical and chemical parameters of the solute and solvent. But as was shown by Schimpf and Giddings (3), none of the existing theories is able to accurately describe the effect of thermal diffusion of polymers in solution. Because of the lack of insight and data, the measurement of thermal diffusion coefficients for various polymer/solvent systems is necessary to increase the understanding of the thermal diffusion process (3). When used in combination with some other technique for the determination of diffusion coefficients, ThFFF is an excellent method for the measurement of thermal diffusion coefficients of polymers in solution (3–7).

However, in ThFFF several complications arise from the fact that a number of important physical parameters are temperature-dependent. Because of the thermal gradient required in ThFFF, these parameters vary across the channel thickness. This makes the theoretical description needed for the conversion of retention data into α/T values more complex. The effect of the temperature dependence of the viscosity and thermal conductivity of the solvent was described by Gunderson et al. (8). But as was shown by Brimhall et al. (4) and Chen et al. (9), the Soret coefficient itself is also temperature-dependent. Although in ThFFF the solute is compressed in a very thin layer at the cold wall, the temperature increment across the solute zone can still be large enough to make the consideration of the temperature dependence of the Soret coefficient necessary. In the most general treatment, the solvent viscosity, the solvent thermal conductivity, and the Soret coefficient are all considered to be temperature-dependent. However, because of the lack of necessary data, it is not always possible to account for the temperature dependence of these parameters. Therefore, it is interesting to know the magnitude of the systematic error when the temperature dependence of one or more of these parameters is neglected in the theoretical description of the separation mechanism.

In this work a numerical fitting method is presented to account for the influence of the temperature change across the solute zone on the Soret coefficient in ThFFF. Furthermore, the effect of the temperature dependence of the solvent viscosity, the solvent thermal conductivity, and the Soret coefficient on the conversion of retention data into thermal diffusion data is studied.

THEORY

Temperature Increment across the Solute Zone

Although it is known that both thermal and ordinary diffusion coefficients are temperature-dependent, we found no literature for ThFFF that handles this problem. The reason for this is that in most cases the solute is compressed in a very thin layer at the cold wall. Therefore, the solute molecules are only subjected to a small temperature range. To get an idea of the magnitude of this temperature increment, one can calculate the temperature increase going from the cold wall to an arbitrarily chosen position in the channel. For the sake of simplicity it is assumed that both the thermal conductivity and the Soret coefficient are temperature-independent. When the distance from the cold wall is equal to the mean layer thickness l, the concentration of the solute has decreased by a factor e^{-1} (0.37). The corresponding temperature increase is equal to

$$T_l - T_c = \frac{\Delta T}{w} l = \Delta T \lambda \tag{1}$$

where T_l and T_c are respectively the temperature at the mean layer thickness of the solute layer and at the cold wall, ΔT is the temperature drop across the channel thickness w, and λ is the dimensionless mean layer thickness.

When the expression for λ in ThFFF (10) is inserted in Eq. (1), the following result is obtained:

$$T_l - T_c = D/D_T \tag{2}$$

where D is the ordinary diffusion coefficient and D_T is the thermal diffusion coefficient.

The magnitude of the temperature range across which the solute is distributed is independent of the temperature difference across the channel thickness. For steep temperature gradients the value of l will be small because the temperature increase per unit distance is large. The only requirement for significant retention is, of course, that $(T_l - T_c)$ must be much smaller than ΔT.

The correlation between D and the molecular weight M of a polymer is often expressed by the empirical relationship $D = AM^{-b}$ (10), where A and b are constants. When this relationship is introduced into Eq. (2) we obtain

$$T_l - T_c = A/D_T M^b \tag{3}$$

For the polymer/solvent systems studied so far, it has been found that D_T is virtually independent of the molecular weight of the polymer (3).

For polystyrene in THF it is known that $D_T = 1 \times 10^{-7}\ \mathrm{cm^2 \cdot s^{-1} \cdot K^{-1}}$, $A = 3.86 \times 10^{-4}$, and $b = 0.57$ (3). It follows that for polystyrene with a molecular weight of 20k, the temperature range is still 13.5 K, where for polystyrene with a molecular weight of 500k, the temperature range is only 2 K. From these results it can be concluded that the temperature dependence of the Soret coefficient can be important to consider, especially for systems in which retention is relatively small (e.g., low molecular weights or small thermal diffusion coefficients).

Velocity Profile of the Carrier Liquid

An expression for the shape of the fluid velocity profile in ThFFF has been derived by Gunderson et al. (8). This treatment is now briefly reproduced and a few minor corrections made.

If uniform flow in the longitudinal dimension of an infinite parallel plate channel is assumed, the equation of motion is given by

$$\frac{d}{dx}\left[\eta(x)\,\frac{dv(x)}{dx}\right] = -\frac{\Delta p}{L} \tag{4}$$

where x is the coordinate in the direction of the channel thickness, $v(x)$ and $\eta(x)$ are, respectively, the liquid velocity and viscosity as functions of x, and Δp is the pressure drop across the channel length L.

When the viscosity of the solvent is constant, the following well-known velocity profile is found:

$$v(x) = 6\langle v\rangle\left[\left(\frac{x}{w}\right) - \left(\frac{x}{w}\right)^2\right] \tag{5}$$

where $\langle v\rangle$ is the mean fluid velocity. However, it is known that the fluid viscosity is strongly temperature-dependent. This temperature dependence can be accounted for by fitting data for fluidity (i.e., the reciprocal of the solvent viscosity) to the following polynomial function (8):

$$1/\eta = a_0 + a_1 T + a_2 T^2 + a_3 T^3 \tag{6}$$

In order to derive the velocity profile, the viscosity as a function of the position x in the channel must be known. Therefore, the temperature profile across the channel thickness must be determined. If the thermal conductivity κ of the solvent is considered to be constant, the temperature profile is linear. However, this is only correct to a first approximation since κ is generally temperature-dependent, expressed according to the equation

$$\kappa = b_0 + b_1(T - T_c) \tag{7}$$

where b_0 is the thermal conductivity at the cold wall temperature.

The term b_1 (equal to $d\kappa/dT$) is assumed to be constant over the considered temperature range. When Eq. (7) is combined with Fouriers law of heat conduction, the following temperature profile is obtained:

$$T(x) = T_c + \frac{-1 + \left[1 + \frac{2x}{w}\frac{b_1}{b_0}\Delta T + \frac{x}{w}\left(\frac{b_1}{b_0}\right)^2 (\Delta T)^2\right]^{1/2}}{b_1/b_0} \tag{8}$$

Substituting Eq. (8) into Eq. (6) would give the desired formula which describes the fluid viscosity as a function of the position in the channel. Because of the complex nature of Eq. (8), the resulting expression for the velocity profile would be very awkward. As was shown by Gunderson et al. (8), a simpler approximation of the temperature profile can be found by expanding the temperature in a Taylor's series around the cold wall temperature:

$$T(x) = T_c + x\left(\frac{dT}{dx}\right)_c + \frac{x^2}{2!}\left(\frac{d^2T}{dx^2}\right)_c + \frac{x^3}{3!}\left(\frac{d^3T}{dx^3}\right)_c + \cdots \tag{9}$$

From Eq. (8) it follows that

$$\left(\frac{dT}{dx}\right)_c = \frac{S}{w} \tag{10}$$

$$\left(\frac{d^2T}{dx^2}\right)_c = -\left(\frac{S}{w}\right)^2 \frac{b_1}{b_0} \tag{11}$$

$$\left(\frac{d^3T}{dx^3}\right)_c = 3\left(\frac{S}{w}\right)^3 \left(\frac{b_1}{b_0}\right)^2 \tag{12}$$

where

$$S = \Delta T + \frac{b_1}{b_0}\frac{(\Delta T)^2}{2} \tag{13}$$

Note that Eq. (12) includes the corrected coefficient of 3 rather than 2, as given in Ref. 8. When Eq. (9) is substituted into Eq. (6), a polynomial relationship in x/w for the solvent fluidity is found. If this polynomial function is truncated after four terms, the fluidity as a function of the channel position is given by

$$\frac{1}{\eta} = d_0 + d_1\left(\frac{x}{w}\right) + d_2\left(\frac{x}{w}\right)^2 + d_3\left(\frac{x}{w}\right)^3 \tag{14}$$

where

$$d_0 = a_0 + a_1 T_c + a_2 T_c^2 + a_3 T_c^3 \tag{14a}$$

$$d_1 = (a_1 + 2a_2 T_c + 3a_3 T_c^2)S \tag{14b}$$

$$d_2 = \left[-\frac{1}{2}a_1\frac{b_1}{b_0} + a_2 - a_2\frac{b_1}{b_0}T_c + 3a_3 T_c - \frac{3}{2}a_3\frac{b_1}{b_0}T_c^2\right]S^2 \tag{14c}$$

$$\begin{aligned} d_3 = \Bigg[&\frac{1}{2}a_1\left(\frac{b_1}{b_0}\right)^2 - a_2\frac{b_1}{b_0} + a_2\left(\frac{b_1}{b_0}\right)^2 T_c \\ &+ a_3 - 3a_3\frac{b_1}{b_0}T_c + \frac{3}{2}a_3\left(\frac{b_1}{b_0}\right)^2 T_c^2\Bigg]S^3 \end{aligned} \tag{14d}$$

The coefficients to the terms in $(b_1/b_0)^2$ of Eq. (14d) have been corrected. The errors in the previously published equation (see Ref. 8) arose from the error made in Eq. (12) pointed out above.

As was shown by Gunderson et al. (8), the use of Eq. (14) led, for ethylbenzene as the solvent, to systematic errors of less than 0.25% in fluidity in the region $0 \leq x/w \leq 0.5$ for $\Delta T = 100$ K. Equation (14) can also be used when the temperature dependence of the thermal conductivity of the solvent is neglected, in which case b_1 is set equal to zero.

With the fluid viscosity expressed as a function of the position in the channel by Eq. (4), it is possible to derive the following equation for the velocity profile:

$$v(x) = \frac{-\Delta p w^2}{L}\left[h_1\left(\frac{x}{w}\right) + h_2\left(\frac{x}{w}\right)^2 + h_3\left(\frac{x}{w}\right)^3 + h_4\left(\frac{x}{w}\right)^4 + h_5\left(\frac{x}{w}\right)^5\right] \tag{15}$$

where

$$h_1 = \theta d_0 \tag{15a}$$

$$h_2 = (d_0 + \theta d_1)/2 \tag{15b}$$

$$h_3 = (d_1 + \theta d_2)/3 \tag{15c}$$

$$h_4 = (d_2 + \theta d_3)/4 \tag{15d}$$

$$h_5 = d_3/5 \tag{15e}$$

$$\theta = -\left[\frac{d_0}{2} + \frac{d_1}{3} + \frac{d_2}{4} + \frac{d_3}{5}\right] \Bigg/ \left[d_0 + \frac{d_1}{2} + \frac{d_2}{3} + \frac{d_3}{4}\right] \tag{15f}$$

From this equation the average fluid velocity can easily be found:

$$\langle v\rangle = \frac{-\Delta p w^2}{L}\left[\frac{h_1}{2} + \frac{h_2}{3} + \frac{h_3}{4} + \frac{h_4}{5} + \frac{h_5}{6}\right] \tag{16}$$

We note that the previously published (8) forms of Eqs. (15) and (16) were in error by the omission of w^2. In Fig. 1 it is demonstrated to what

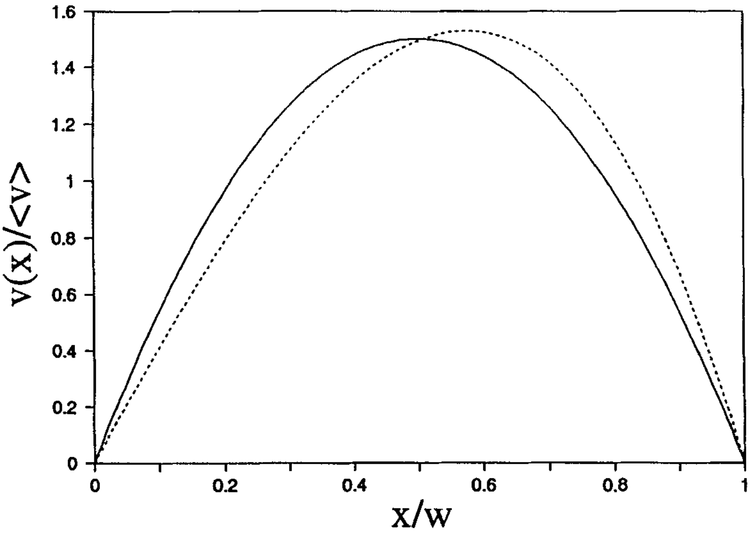

FIG. 1 Velocity profiles calculated for ethylbenzene for $T_c = 293$ K and $\Delta T = 100$ K. Profiles are drawn for the assumption of constant η and κ (full line), and for temperature-dependent η and κ (dashed line).

extent the velocity profile for ethylbenzene (as an example) is influenced by the temperature dependence of the fluid viscosity and thermal conductivity. The parameters describing this temperature dependence are given in Table 1. From Fig. 1 it can be concluded that the temperature dependence of the fluid viscosity has a significant influence on the shape of the velocity profile. The effect of the temperature dependence of the thermal conductivity was found to be relatively insignificant. If the solvent viscosity is considered to be constant, systematic errors of up to 35% are made in the prediction of the fluid velocity near the cold wall. Neglecting the temperature dependence of the thermal conductivity leads in this case to corresponding systematic errors of less than 1% for ethylbenzene. These results are typical of most organic solvents.

Concentration Profile of the Solute

The concentration profile in ThFFF can be determined by solving the following differential equation:

$$\frac{1}{c}\frac{dc}{dx} = -\left(\frac{\alpha}{T}\right)\frac{dT}{dx} \tag{17}$$

where c is the concentration as a function of the position in the channel and α is the Soret coefficient. The term α/T is the ratio of the thermal and ordinary diffusion coefficients. If this ratio is considered to be constant, the concentration profile is obtained as

$$c(x) = c_0 \exp[-(\alpha/T)(T(x) - T_c)] \tag{18}$$

where c_0 is the concentration at the cold wall.

To obtain the concentration as a function of the position within the channel, the temperature profile must be known. If the thermal conductiv-

TABLE 1

Empirical Constants Describing the Temperature Dependence of the Viscosity and Thermal Conductivity for THF (8, 13) and Ethylbenzene (4, 14)

	Ethylbenzene	THF
a_0	2892.923	7622.73
a_1	−35.176	−88.933
a_2	0.1284	0.3344
a_3	-8.395×10^{-5}	-3.259×10^{-4}
κ(293 K) ($\mathrm{J{\cdot}m^{-1}{\cdot}s^{-1}{\cdot}K^{-1}}$)	0.1321	0.1398
b_1 ($\mathrm{J{\cdot}m^{-1}{\cdot}s^{-1}{\cdot}K^{-2}}$)	-2.437×10^{-4}	-1.989×10^{-4}

ity of the solvent is taken as a constant, the temperature profile is linear, as pointed out earlier. However, if the thermal conductivity is temperature-dependent, Eq. (8) must be used. The influence of this temperature dependence on the concentration profile of polystyrene 20k in ethylbenzene is demonstrated in Fig. 2. It is clear that the temperature dependence of the thermal conductivity has a stronger influence on the concentration profile of the solute than on the velocity profile of the solvent. If the thermal conductivity of the solvent is considered to be constant, systematic errors up to 20% can be made in the prediction of the concentration of the solute.

However, as was already shown, the ratio of the thermal and ordinary diffusion coefficients is also temperature-dependent. This temperature dependence can be accounted for by using the following empirical relationship:

$$\alpha/T = e_0 + e_1T + e_2T^2 \tag{19}$$

The temperature dependence of α/T can be determined by measuring the retention ratio of the polymer/solvent system at various cold wall temperatures. For the conversion of this retention data into α/T values, it has been assumed in previous work that the temperature drop across the solute

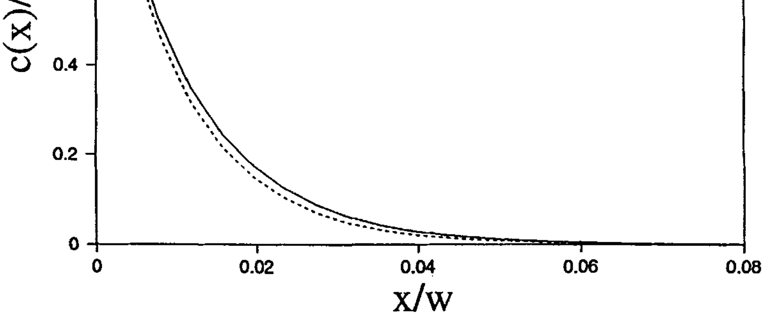

FIG. 2 Concentration profiles for polystyrene 20k in ethylbenzene (T_c = 293 K, ΔT = 100 K, $D_T = 9.5 \times 10^{-8}\,\text{cm}^2\cdot\text{s}^{-1}\cdot\text{K}^{-1}$, $D = 1.1 \times 10^{-6}\,\text{cm}^2\cdot\text{s}^{-1}$) calculated for constant and temperature-dependent κ (full and dashed lines, respectively). In each case, α/T is assumed constant.

zone can be neglected. Each measurement then corresponds to a constant α/T value at some fixed system temperature. This fixed temperature has been assumed to correspond to the cold wall temperature or, alternatively, to the temperature at the center of gravity of the solute zone (4). However, this is only correct to a first approximation. When the influence of the temperature drop across the solute zone on α/T is taken into account, the concentration profile given in Eq. (20) is found. This equation can be derived with the use of Eqs. (17) and (19).

$$c(x) = c_0 \exp\left(-\left[e_0(T(x) - T_c) + \frac{e_1}{2}(T(x)^2 - T_c^2) + \frac{e_2}{3}(T(x)^3 - T_c^3)\right]\right) \tag{20}$$

Once again the temperature profile is required to obtain the concentration as a function of the position in the channel. If the thermal conductivity of the solvent is considered to be constant, the concentration profile is given by

$$c(x) = c_0 \exp\left(-\left[f_1 \Delta T\left(\frac{x}{w}\right) + f_2(\Delta T)^2\left(\frac{x}{w}\right)^2 + f_3(\Delta T)^3\left(\frac{x}{w}\right)^3\right]\right) \tag{21}$$

where

$$f_1 = e_0 + e_1 T_c + e_2 T_c^2 \tag{21a}$$

$$f_2 = \frac{e_1}{2} + e_2 T_c \tag{21b}$$

$$f_3 = e_2/3 \tag{21c}$$

However, if the temperature dependence of thermal conductivity is considered, the following concentration profile is found:

$$c(x) = c_0 \exp(-[f_1 G + f_2 G^2 + f_3 G^3]) \tag{22}$$

where

$$G = \frac{-1 + \left[1 + \frac{2x}{w}\frac{b_1}{b_0}\Delta T + \frac{x}{w}\left(\frac{b_1}{b_0}\right)^2 (\Delta T)^2\right]^{1/2}}{b_1/b_0} \tag{22a}$$

Retention Ratio

The retention ratio in FFF can generally be expressed as (11)

$$R = \frac{\langle cv \rangle}{\langle c \rangle \langle v \rangle} \tag{23}$$

where $\langle \ \rangle$ denotes averaging over the cross-section of the channel. This equation ultimately links the measured retention ratio to the Soret coefficient, from which it is possible to find the thermal diffusion coefficient. To obtain a relationship between R and the Soret coefficient, the temperature dependence of the solvent viscosity, solvent thermal conductivity, and α/T must be considered. Only if the temperature dependence of the solvent viscosity is ignored, and all other parameters are considered constant, does Eq. (23) yield an analytical solution. In this case the following well-known equation is found:

$$R = 6\lambda[\coth(1/2\lambda) - 2\lambda] \tag{24}$$

In every other case, numerical integration is necessary.

If the influence of the temperature drop across the solute zone on α/T is taken into account, Eq. (20) in combination with Eq. (23) will yield a complicated expression for R as a function of the parameters e_0, e_1, e_2, and the cold wall temperature. For each combination of e-values it is then possible to calculate the theoretically expected retention ratio for a given cold wall temperature. The estimation of e_0, e_1, and e_2 for some polymer/solvent system requires measurement of retention ratios at a minimum of three cold wall temperatures. The interpretation of such measurements in terms of e_0, e_1, and e_2 cannot be performed via explicit expressions. It can only be done with the use of a fitting procedure (e.g., simplex optimization), finding those e-values for which the difference between the calculated and measured retention ratios is minimal. The temperature dependence of α/T is thereby described as accurately as possible. For the determination of the best-fit temperature dependence of α/T, the following scheme was used:

1. The retention data of polystyrene in ethylbenzene and in THF for different cold wall temperatures was taken from Ref. 4 and Ref. 9, respectively.
2. α/T was first assumed to be independent of T across the solute zone thickness in order to obtain initial estimates for α/T values for the different cold wall temperatures from the measured retention ratios. The temperature at the center of mass of each of the solute zones was

calculated (4), and Eq. (19) was used to fit these data. The resultant e-values served as starting parameters for the fitting process.

3. The fitting process was carried out to find the combination of e-values for which the temperature dependence of α/T was described as accurately as possible.

When some other technique for the determination of the temperature dependence of the ordinary diffusion coefficient is used, it is possible to determine the temperature dependence of the thermal diffusion coefficient from these e-values.

METHODS AND PROCEDURES

All computer programs were written in Turbo Pascal 6.0 (Borland International, Scotts Valley, California, USA). For the various numerical integrations, a simple routine based on Gaussian quadratures was taken (16). As a fitting procedure, a modified simplex method was used (12). The numerical integration routine was tested by comparing it with a more sophisticated, time-consuming integration routine which used a variable step width. No significant differences were observed. The fitting procedure was tested with the use of artificial data sets containing data points which were calculated for a special combination of e-values. Slightly different e-values were given as starting values. The modified simplex method found the original combination of e-values without difficulty.

To study the importance of the effect of the temperature gradient on the solvent viscosity, solvent thermal conductivity, and α/T, a total of eight methods was developed. These methods are coded with three symbols to indicate which assumptions were made concerning the influence of the temperature gradient on the three parameters of interest. When the temperature dependence of the viscosity is taken into account, the symbol η is present in the code. For the thermal conductivity, the symbol κ is included. The symbol α indicates that the influence of the temperature increment across the solute zone on α/T is considered. If the effect of the temperature gradient on one of these parameters is neglected, an asterisk is shown. Thus, in method [$\eta\kappa\alpha$] all temperature effects are considered, while for method [***] none of the effects are taken into account.

As was noted earlier, the effect of the temperature gradient on α/T can only be determined if the retention ratio is measured at different cold wall temperatures. Such measurements have been carried out for polystyrene in the organic solvents ethylbenzene (4) and THF (9). An overview of the retention data for these two systems is given in Tables 2 and 3. To account for the temperature dependence of the solvent viscosity and thermal con-

TABLE 2
Retention Ratio Data for Polystyrene in Ethylbenzene at Different Cold Wall Temperatures (w = 254 μm, ΔT = 40 K) (4)

	M			
T_c (K)	21,000	51,000	97,000	160,000
269	0.761	0.543	0.371	0.286
270	0.733	0.534	0.380	0.302
275			0.421	
289	0.800	0.629	0.464	0.350
303	0.826		0.497	0.385
308		0.679		
310	0.809	0.657	0.493	
333	0.909	0.772	0.630	0.536
348	0.896	0.815	0.649	0.551
363		0.871	0.725	0.635
379		0.887	0.765	
380				0.633
393		0.886	0.773	0.692
408			0.819	0.772
409		0.920		
423		0.934	0.840	
424				0.754

TABLE 3
Retention Ratio Data for Polystyrene in THF at Different Cold Wall Temperatures (w = 76 μm, ΔT = 30 K) (9)

	M			
T_c (K)	233,000	400,000	575,000	900,000
291	0.477	0.434	0.374	0.262
301	0.526	0.471	0.380	0.314
311	0.577	0.500	0.428	0.339
321	0.632	0.550	0.468	0.367
331	0.654	0.567	0.485	0.405
341	0.680	0.607	0.527	0.420

ductivity, certain empirical constants must be known. For THF and ethylbenzene, the values of these constants are given in Table 1.

RESULTS AND DISCUSSION

The results obtained with the most general method [$\eta\kappa\alpha$] are given for polystyrene in ethylbenzene in Table 4 and for polystyrene in THF in Table 5. For these results, method [$\eta\kappa^*$] was used to find the starting values for the fitting procedure. It must be noted that the polynomial functions describing the temperature dependence of α/T are only valid within the range of cold wall temperatures of the measurements. For polystyrene in THF, the cold wall temperature ranged from 291 to 341 K, while for polystyrene in ethylbenzene this range was from 269 to 424 K.

The fitting process minimizes the sum of squared differences between the calculated and measured retention ratios for the different cold wall temperatures. The ratio of this sum of squared differences before and after the fitting process is given in the last columns of Tables 4 and 5. This ratio gives an indication of the improvement in the theoretical description of the system when the influence of the temperature gradient on α/T is taken into account. This ratio is expected to go to unity with increasing molecular weight because high M polymers occupy a narrower temperature range (see Eq. 3). Except for polystyrene having M = 900k, this trend can clearly be seen in Table 5. This trend is not shown in Table 4, however. Because of the lower molecular weights of the polystyrenes used for the measurements in ethylbenzene, it was also expected that the ratios given in Table 4 should be larger than the ratios in Table 5. This effect also is not apparent. The reason for these discrepancies can be found when the data sets given in Tables 2 and 3 are compared. The

TABLE 4

Polynomial Coefficients Describing the Temperature Dependence of α/T for Polystyrene in Ethylbenzene Obtained by Method [$\eta\kappa\alpha$]. Starting Values for the Fitting Process Were Found with the Use of Method [$\eta\kappa^*$]. The SSD Ratio is the Ratio of the Sum of Squared Differences (between the measured and calculated retention ratios) of Method [$\eta\kappa^*$] and [$\eta\kappa\alpha$]

M	e_0	e_1	e_2	Sum of squared differences ratio
21,000	0.325	−9.041*e*-4	4.206*e*-7	1.16
51,000	0.986	−4.132*e*-3	4.541*e*-6	1.05
97,000	1.456	−6.078*e*-3	6.721*e*-6	1.13
160,000	2.135	−9.241*e*-3	1.058*e*-5	1

TABLE 5
Polynomial Coefficients Describing the Temperature Dependence of α/T for Polystyrene in THF Obtained Using Method [$\eta\kappa\alpha$]. Starting Values for the Fitting Process Were Found with Method [$\eta\kappa^*$]. The SSD Ratio Is the Same as in Table 4

M	e_0	e_1	e_2	Sum of squared differences ratio
233,000	4.742	−2.556*e*-2	3.583*e*-5	1.90
400,000	2.545	−1.167*e*-2	1.438*e*-5	1.24
575,000	2.395	−9.764*e*-3	1.057*e*-5	1.05
900,000	10.512	−5.805*e*-2	8.314*e*-5	1.17

data for polystyrene in ethylbenzene consists of more than one series of measurements (4). This has led to some inconsistencies in this data set. The retention ratios measured at a cold wall temperature of 310 K are lower than expected. The data set for polystyrene in THF does not contain such obvious discrepancies, and the fitting procedure reduces the sum of the square of the residuals in R to a greater extent.

It is very difficult to translate the standard deviation in the measurements to a standard deviation of the determination of α/T as a function of the temperature. This is due to the fact that only a specific combination of the three e-values is of importance. The fitting process can only lead to meaningful results if the data sets are relatively precise and free of systematic errors.

The effect of the fitting procedure is demonstrated in Figs. 3 and 4. In Fig. 3, α/Ts for polystyrene 233k in THF determined via three methods are plotted as functions of temperature. The top line was found using method [$\eta\kappa\alpha$]. The other two lines correspond to two variants of method [$\eta\kappa^*$], where the constant α/T values were coupled to either the cold wall temperature T_c or to the temperature T_{cg} at the center of gravity of the solute zone (for all other results obtained with method [$\eta\kappa^*$], this latter definition was used). The effect of the fitting procedure can clearly be noticed, especially for the lower temperatures. Accounting for the effect of the temperature gradient on α/T leads to higher α/T values. When α/T is considered to be constant across zone thickness, it can better be linked to the temperature in the center of gravity of the solute zone than to the cold wall temperature. When the cold wall temperature is assumed, even lower α/T values are found.

In Figure 4 the percentage differences of the α/T values before and after the optimization are shown for the measurements of polystyrene in THF. This figure demonstrates that the effect of the temperature dependence of α/T is more important for low molecular weights and low temperatures.

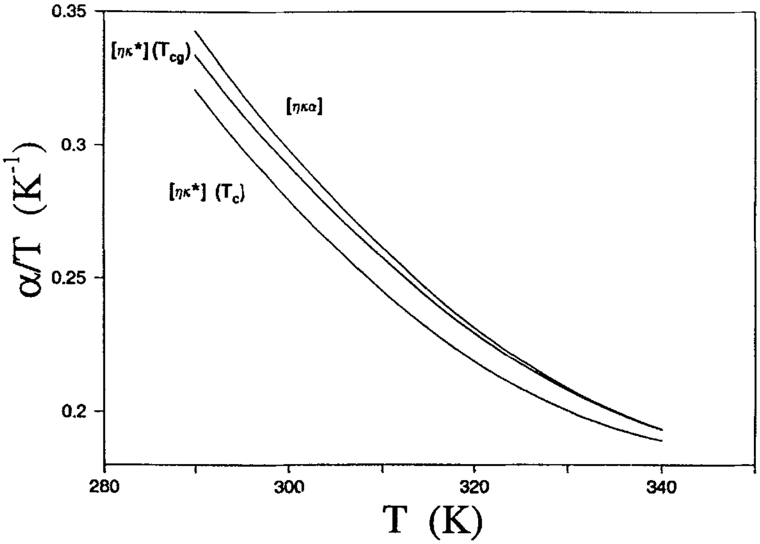

FIG. 3 Results for the determination of α/T as a function of temperature for polystyrene 233k in THF using method [ηκα] and method [ηκ*] based on both T_{cg} and T_c as explained in the text.

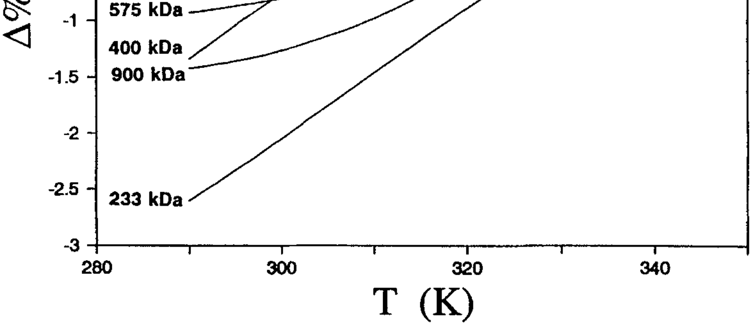

FIG. 4 Percentage differences between α/T values obtained with method [ηκ*] and method [ηκα] for polystyrene in THF for M = 233k, 400k, 575k, and 900k, as labeled.

Figure 5 illustrates the effect of the temperature dependence of the solvent viscosity and solvent thermal conductivity on the determination of α/T. Polystyrene 233k in THF was taken as an example. Four methods were compared for evaluating the effect of the temperature gradient on α/T. From this figure it can be seen that the temperature dependence of the viscosity is of more importance than the temperature dependence of the thermal conductivity. Furthermore, neglecting the temperature dependence of the viscosity leads to higher α/T values, while neglecting the temperature dependence of the thermal conductivity leads to slightly lower α/T values.

To compare all eight methods, the following procedure was carried out. The polynomial function for α/T in terms of T found with the use of method [ηκα] was compared with the polynomial functions found when using the other seven methods. Method [ηκα] is the most general method; comparing the other methods with method [ηκα] thus gives an indication of the systematic error made when some of the parameters are considered to be constant. For polystyrene 233k in THF, the results are illustrated in Fig. 6. In this figure the percentage differences in α/T values between method [ηκα] and the other seven methods are plotted as functions of temperature. From this figure it can be concluded that the use of methods [*κ*], [**α], and [*κα] leads to unacceptable systematic errors in the determination of

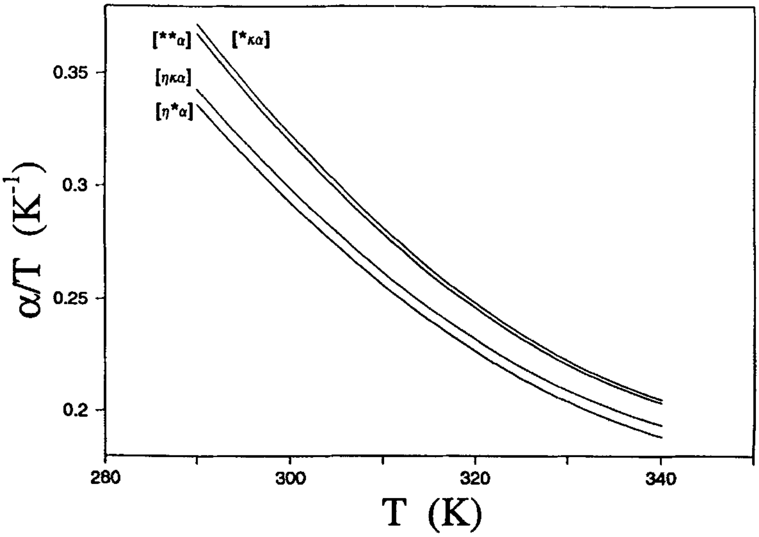

FIG. 5 Results obtained for α/T as a function of temperature for polystyrene 233k in THF using methods [*κα], [**α], [ηκα], and [η*α].

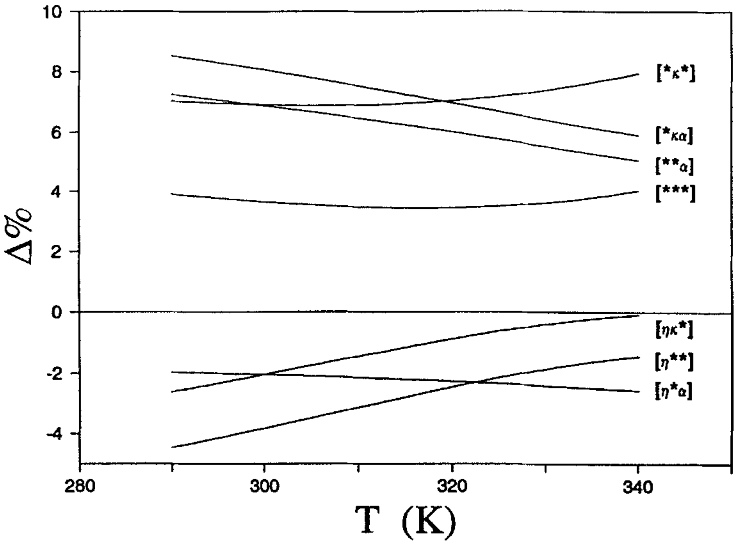

FIG. 6 Percentage differences between α/*T* values obtained via the most general method [ηκα] and the other methods for polystyrene 233k in THF.

α/*T*. All other methods are worth considering. Neglecting the temperature dependence of the thermal conductivity (method [η*α]) leads, in this particular sample, to a systematic error of about 2%, which is constant throughout the temperature range. If α/*T* is considered to be constant (method [ηκ*]), a maximum systematic error of about 3% is observed for the lower temperatures. For higher temperatures the magnitude of the systematic error decreases; this can also be seen in Fig. 3. For method [η**] (where only the solvent viscosity is considered to be temperature-dependent), the same trend is observed as for method [ηκ*]. The only difference is that in this case the systematic error is somewhat larger (a maximum of about 5%). Neglecting the effect of the temperature gradient on all three parameters (method [***]) leads to surprisingly good results. For this method a systematic error of about 4% is made, which is constant throughout the considered temperature range. The reason for this is clear from the results obtained using the other methods. As was shown in Fig. 3, neglecting the effect of the temperature gradient on α/*T* leads to slightly lower α/*T* values. The same can be said when the solvent thermal conductivity is considered to be constant (see Fig. 5). However, omitting the temperature dependence of the solvent viscosity leads to considerably higher α/*T* values. When the effect of the temperature gradient on all three parameters is neglected, the two smaller effects (temperature dependence of thermal conductivity and of α/T) partly counteract the large effect of the temperature dependence of the solvent viscosity.

From these results it can be concluded that the temperature dependence of the solvent viscosity is important to consider. Although the effects of the temperature gradient on the thermal conductivity and α/T are of only minor importance, they both counteract the effect of the temperature dependence of the solvent viscosity. Therefore, the results obtained with method [***] are still quite acceptable. This can be an important consideration when thermal diffusion measurements are carried out in complicated systems, such as mixed organic solvents (15), for which no data are available on the temperature dependence of the thermal conductivity and viscosity.

CONCLUSIONS

With the use of a modified simplex optimization and a numerical integration routine, it is possible to account for the influence of the temperature drop across the solute zone on α/T.

The systematic error that is made when α/T is considered to be constant is larger for systems in which retention is low (e.g., for low molecular weights or small thermal diffusion coefficients). The magnitude of the systematic error can be large enough to make the consideration of the effect of the temperature gradient on α/T necessary (even for polystyrene 233k in THF a maximum error of 3% was found).

The temperature dependence of the solvent viscosity is of much more importance than the temperature dependence of the thermal conductivity. Neglecting the temperature dependence of the viscosity leads for polystyrene 233k in THF to a systematic error of about 8% in the determination of α/T. If the temperature dependence of the solvent thermal conductivity is neglected, this alone leads to a systematic error in α/T of about 2–3% for the same system.

For the data sets studied, the effect of the temperature dependence of the viscosity is counteracted by the effect of the temperature gradient on the thermal conductivity and α/T. This means that when all three parameters are considered constant, the determination of α/T remains quite acceptable (a systematic error of about 4% was found for polystyrene 233k in THF).

SYMBOLS

α	Soret coefficient
c	concentration ($\text{mol}\cdot\text{L}^{-1}$)

c_0	concentration at the cold wall ($\mathrm{mol{\cdot}L^{-1}}$)
Δp	pressure drop across channel length (Pa)
ΔT	temperature difference across channel thickness (K)
D	diffusion coefficient ($\mathrm{m^2{\cdot}s^{-1}}$)
D_T	thermal diffusion coefficient ($\mathrm{m^2{\cdot}s^{-1}{\cdot}K^{-1}}$)
η	solvent viscosity (Pa·s)
κ	solvent thermal conductivity ($\mathrm{J{\cdot}m^{-1}{\cdot}s^{-1}{\cdot}K^{-1}}$)
κ_c	solvent thermal conductivity at the cold wall ($\mathrm{J{\cdot}m^{-1}{\cdot}s^{-1}{\cdot}K^{-1}}$)
λ	dimensionless characteristic height of the solute layer
l	characteristic height of the solute layer (m)
L	channel length (m)
M	molecular weight (Da)
R	retention ratio
T	temperature (K)
T_c	temperature at the cold wall (K)
T_l	temperature at the characteristic height of the solute layer (K)
v	linear fluid velocity ($\mathrm{m{\cdot}s^{-1}}$)
$\langle v \rangle$	mean linear fluid velocity ($\mathrm{m{\cdot}s^{-1}}$)
w	channel thickness (m)
x	coordinate in the direction of the channel thickness (m)

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