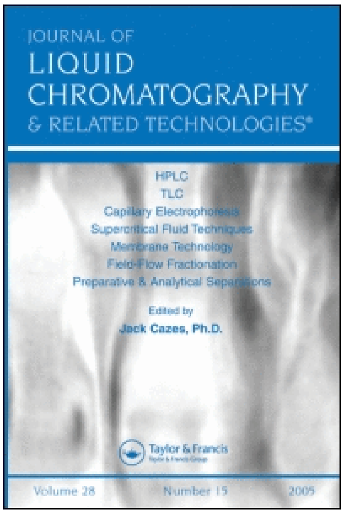

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EVALUATION OF THE SORET COEFFICIENT FOR POLYSTYRENE IN DECALIN BY MEANS OF THERMAL FIELD-FLOW FRACTIONATION

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ABSTRACT

One of the most appealing features of FFF (Field-Flow Fractionation) techniques is their capability of easily finding out direct mathematical relationships between the retention parameter and physico-chemical parameters of the analytes. In the case of thermal FFF applied to macromolecules in solution, these parameters are the Soret coefficient and the molar mass. In this work, a rich set of retention data for polystyrene in a mixture of *cis* and *trans* decalin, in a wide range of temperatures and molar masses, is used for finding out an empirical relationship between Soret coefficient, temperature, and molar mass using a refined approach of handling thermal FFF data. This law is then statistically tested and very good agreement between experimental and predicted values of Soret coefficient is found. The importance of this law lies in the fact that it makes possible a truly universal calibration of the polystyrene-decalin system on any thermal FFF apparatus in the investigated ranges of temperatures and molar masses. The thermodiffusion coefficient of polystyrene in *cis* + *trans* decalin is evaluated for various molar masses at the temperature of 333 K and a slight dependence of this parameter on molar mass at that temperature is observed.

INTRODUCTION

Thermal Field-Flow Fractionation (ThFFF) has been proven to be a powerful method for separation and characterization of macromolecules and particles.[1-4] It is based on Soret coefficient (s_T), that is the ratio of thermodiffusion coefficient D_T (cm^2 s^{-1} K^{-1}) to the ordinary diffusion coefficient D (cm^2 s^{-1}). The Soret coefficient reflects the tendency for the components of a solution to differentially migrate into regions at different temperature. The advantages of this technique with respect to classical size exclusion separation methods have been reported.[5-6] In particular, a well defined geometrical shape of the fractionating channel allows one to derive a precise relationship between retention, Soret effect, and thermal gradient.

The theory of FFF exactly derives the retention parameter λ from retention data. In ThFFF λ is approximately inversely proportional to the Soret coefficient; therefore, the power dependence between s_T and the molar mass results in an approximate linear dependence between the logarithm of the retention factor λ and the logarithm of the molar mass. This approach was used to interpret data in a number of papers.[7-11] However, this approach is only an approximated one because it is based on a mean value of λ across the whole channel thickness. Recently, a more refined theoretical and numerical handling of the physical aspects of ThFFF was put forward.[4,12-14] It takes into account not only the temperature dependence of viscosity and thermal conductivity, already previously considered,[8,11,15] but also, even more important, of the Soret coefficient. All these theoretical advancements make ThFFF an appealing physico-chemical method for experimental measurements of the Soret coefficient, with distinct advantages: low injected quantities are needed (as far as few micrograms), the experimental measurement is rapid (typically in the 5-30 min range) and can be easily repeated, wide temperature and molar mass ranges can be exploited, the method is suitable for impure, mixed or, in a certain extent, unstable compounds. Moreover, commercial equipment is available.

The need to collect data of Soret coefficient for a chosen combination of polymer and solvent in a widely extended range of temperature and molar mass comes from several questions of both theoretical and practical relevance. First, the determination of the polymer molar mass and temperature dependence of the Soret coefficient allows for optimizing their separation and for establishing a basis for a universal calibration[5] of the ThFFF method for these polymers. Second, the knowledge of the Soret coefficient is important for several purposes, *e. g.* for setting up preparative separation methods like the thermogravitational one and for engineering purposes, like for instance, studies of instabilities. Moreover, the Soret effect is related in a complex way to both thermodynamic and essentially irreversible quantities.[16] New experimental data are thus useful for any progress in theoretical understanding of these basic irreversible processes.

In this paper, theoretical handling previously presented by some authors,[4,13] fully describing the complexity of the ThFFF process, is applied to a very extended set of ThFFF retention data for polystyrene in *cis* + *trans* decalin in a wide range of temperature and molar mass. These data are employed for a practical test for determining a model equation to relate the Soret coefficient to molar mass and temperature. Below, the different levels of the mathematical approach to be employed are reported.

Decalin has been chosen as a solvent in this work for its interesting characteristics: low toxicity, high boiling point, and hence suitability for dissolving high molar mass polymers at high temperature, high dissolving power (even with respect to polyolefins), good selectivity in ThFFF.[11] Moreover, the *cis* + *trans* mixture has been chosen because it is commercially available at a significantly lower price than the single isomers.

THEORY

Separation in ThFFF takes place within a very thin ribbon-like open channel clamped between two metal bars between which a temperature difference is applied. Due to the very low thickness of the separation channel, a very strong thermal gradient is set up (nearly 4000 K cm^{-1}) and hence macromolecules are exposed to a very strong Soret effect, which makes them migrate to the accumulation wall. Due to the very low distance between hot and cold walls, when macromolecules are introduced in the channel they very rapidly move along the thickness and very soon reach a stationary state distribution. This fact is an important distinctive feature with respect to other classical techniques based on thermophoretic effects:[17] in fact, those techniques often require very long times for equilibration that is for being allowed to perform measurements.

The parameter governing retention in ThFFF is the retention factor λ and is related to the distance with respect to the accumulation wall (x), that the analyte keeps during the separation process. The fundamental equation to be solved in order to directly relate retention to Soret coefficient, s_T (K^{-1}), is:

$$R = \frac{1}{w}\int_0^w \frac{c}{<c>} \frac{v}{<v>} dx \tag{1}$$

where R is the analyte relative velocity, that is the ratio of the void time t_0 to the retention time t_R, c is the concentration, is the flow velocity and w is the channel thickness. Terms in brackets (< >) indicate average values across the channel section. Solution of Eq. 1 can be carried out if both the concentration profile and the velocity profile are calculated. This is possible[4] and can be done in ThFFF at three different levels of approximation, which differ from each other, as for the accuracy with which the influences of temperature on viscosity, thermal conductivity, and Soret coefficient itself are taken into account.

Approximated Approach[4]

If the influences of temperature on viscosity and thermal conductivity are ignored the velocity profile is parabolic. If the influences on Soret coefficient and density are ignored too the concentration profile is exponential:

$$c = c_0 \quad e^{-\frac{x}{\lambda w}} \tag{2}$$

where c_0 is the value of c at the accumulation wall, and λ is given by:

$$\lambda = \frac{D}{D_T \Delta T} = \frac{1}{s_T \quad \Delta T} \tag{3}$$

where ΔT is the temperature difference between the upper (hot) and lower (cold) wall. Solution of Eq. 1 brings to:

$$R = 6\lambda\left[\coth\left(\frac{1}{2\lambda}\right) - 2\lambda\right] \tag{4}$$

Hence, by combining Eqs. 3 and 4, it is easy to calculate the Soret coefficient from the measured R.

Partially Approximated Approach[4]

Many authors[7-8,10-11] solved Eq. 1 taking into account only the influence of temperature on viscosity and thermal conductivity, that is, on the deformation of the velocity profile with respect to the parabolic case. This deformation can be quantified by introducing a flow distortion parameter, ν, such that the slope of the velocity profile at the accumulation wall is $(1 + \nu)$ times that of a parabolic profile for the same flow rate. In this case, Eq. 4 changes into:

$$R = 6\lambda\left\{\nu + (1-6\lambda\nu)\left[\coth\left(\frac{1}{2\lambda}\right) - 2\lambda\right]\right\} \tag{5}$$

Calculation of Soret coefficient from retention ratio is now possible by combining Eqs. 3 and 5.

Refined Approach[4,13]

The Soret coefficient, too, depends on temperature and, hence, Eqs. 2 and 3 are not exact. Then, a thermal FFF run is not associated to single values of s_T and λ but to ranges of values of s_T and λ. Still, one can apply the classical approaches and determine, from retention time, one apparent value of λ , λ_{app}, which is expected to lie within the range of λ values inside the channel. Martin *et al.*[13] have shown that, provided that the variation of λ across the channel can be considered as linear, this apparent value obtained by applying Eq. 5 is found at a position, x_{eq}, in the channel given by:

$$\frac{x_{eq}}{w} = 2\ \lambda_{app} - 2.1365\ (1+2\nu)\ \lambda_{app}^2 - 6.1678\ (2-\nu)\ \lambda_{app}^3 \tag{6}$$

Since the temperature profile $T(x)$ is known, and given by the following equation:[4]

$$T = T_C + \frac{1}{\omega_C}\left(\sqrt{1+2\omega_C\Delta T\left(1+\frac{\omega_C\Delta T}{2}\right)\frac{x}{w}} - 1\right),\ \omega_C = \frac{1}{\kappa_C}\frac{d\kappa}{dT} \tag{7}$$

where T_C and κ_C are the temperature and the thermal conductivity at the accumulation wall, it is easy to calculate T_{eq}, that is the temperature with which λ_{app} is associated, by substituting in Eq. 7 the value of x_{eq} obtained from Eq. 6. Finally, it is possible to calculate the Soret coefficient using the following equation:[18]

$$s_T(T_{eq}) = \frac{1}{\lambda_{app}\left.\frac{dT}{d(x/w)}\right|_{T_{eq}}} - \gamma(T_{eq}) \tag{8}$$

where $\gamma\,(K^{-1})$ is the thermal expansion coefficient of the solvent.

It must be pointed out that all these treatments hold true for pure solvents. For mixed solvents, such as the case of *cis* + *trans* decalin technical mixture here employed, compositional changes may appear due to the Soret effect of the solvent mixture itself. Unfortunately, the treatment of thermodiffusion of a ternary mixture (solute and binary solvent mixture) is a topic of high complexity which has not been satisfactorily solved up to now. Still, one may expect, on the basis of data published for simple solvent mixtures, that the effect is small in the present experimental conditions. Moreover, this present handling does not take into account such a complexity; nonetheless, the results of this study can be applied under similar experimental conditions as far as temperature and thermal gradient are concerned.

NUMERICAL HANDLING

Viscosity

The solvent viscosity profile $\eta(x)$ is calculated by combining Eq. 7 with the following one:

$$\frac{1}{\eta} = p_0 + p_1 \quad T + p_2 \quad T^2 + p_3 \quad T^3 \tag{9}$$

The coefficients p_i in the case of decalin can be found in literature.[19] In fact, only coefficients for pure *trans* and pure *cis* decalin are available; however, these coefficients allow for the calculation of $\eta(T)$ for each pure solvent, and the $\eta(T)$ for a mixture of *cis* and *trans* decalin can be determined by applying the Arrhenius equation:[20]

$$\log \eta_{\text{mixture}} = X_{\text{cis}} \log \eta_{\text{cis}} + X_{\text{trans}} \log \eta_{\text{trans}} \tag{10}$$

where X is the molar fraction. Once $\eta(T)$ for the mixture is determined, the relative p_i coefficients to be put in Eq. 9 can be easily determined by means of a polynomial regression. Table 1 reports the p_i coefficients for the pure solvents (found in literature) and for the mixture used here (calculated).

Thermal Conductivity

Thermal conductivity of the solvent is evaluated by means of the following empirical equation:

$$\kappa_C = q_0 + q_1(T_C - T_0) \tag{11}$$

where q_0 is the thermal conductivity at temperature T_0.

Table 1

Parameters for Calculating $1/\eta(T)$ and $\kappa(T)$

Solvent	p_0 (cP^{-1})	p_1 ($cP^{-1}K^{-1}$)	p_2 ($cP^{-1}K^{-2}$)	p_3 ($cP^{-1}K^{-3}$)	q_0 (erg $cm^{-1}s^{-1}K^{-1}$)	q_1 (erg $cm^{-1}s^{-1}K^{-2}$)
Cis decalin	6.41	$-6.02\ 10^{-2}$	$1.75\ 10^{-4}$	$-1.37\ 10^{-7}$	$1.40\ 10^{4}$	-9
Trans decalin	4.64	$-4.58\ 10^{-2}$	$1.38\ 10^{-4}$	$-1.05\ 10^{-7}$	$1.40\ 10^{4}$	-9
Cis + trans decalin	5.59	$-5.37\ 10^{-2}$	$1.58\ 10^{-4}$	$-1.23\ 10^{-7}$	$1.40\ 10^{4}$	-9

The parameters q_i for *cis+trans* decalin were computed using experimental data from previous studies.[21] They were found identical for the two isomers and are reported in Table 1.

Density and Void Time

The solvent density $\rho(T)$ is evaluated by means of the Hankinson-Brobst-Thomson method.[22] $\rho(T)$ is used for calculating γ by means of the following equation:

$$\gamma(T) = -\frac{1}{\rho(T)}\frac{d\rho(T)}{dT} \tag{12}$$

and also for correcting the void time t_0 for the effect of temperature on density. In fact, void time is evaluated, as usual in FFF, by measuring the elution time of an unretained sample at room temperature (T_{room}). The exact evaluation of void time to be used in the computation of R in different temperature conditions has been performed by applying the following correction:

$$t_0 = t_0(T_{room})\frac{\int_{T_C}^{T_C+\Delta T}\rho(T)\ dT}{\rho(T_{room})\ \Delta T} \tag{13}$$

Flow Distortion Parameter ν

The ν coefficient is calculated by means of the following algorithm:[4]

$$\nu = \frac{h_1}{6\sum_{i=1}^{5}\frac{h_i}{i+1}} - 1 \tag{14}$$

$$h_i = \frac{1}{i}\left(d_{i-2} + \theta \ \ d_{i-1}\right) \ \ i = 1,\ldots,5 \ \ d_{-1} = d_4 = 0 \ \ d_0 = 1 \tag{15}$$

$$\theta = -\frac{\sum_{i=0}^{3}\frac{d_i}{i+2}}{\sum_{i=0}^{3}\frac{d_i}{i+1}} \tag{16}$$

$$\frac{\frac{\eta_C}{\eta} - 1}{x/w} = d_1 + d_2 \ \ (x/w) + d_3 \ \ (x/w)^2 \tag{17}$$

where $\eta_C = \eta(T_C)$ and the d_i coefficients in Eq. 17 are computed by performing a polynomial regression analysis on a set of data (x, $\eta(x)$) with x ranging from 0 to w, obtained from the correspondent set of data (T, $\eta(T)$) with T ranging from T_C to $T_C + \Delta T$.

Soret Coefficient

The procedure consists of the following steps:

Collect a large number of retention data for various cold wall temperatures and various molar masses M.

For each experimental (R, T_C, ΔT, M) set, calculate T_{eq} and $s_T(T_{eq})$.

For each molar mass, plot $s_T(T_{eq})$ vs. T_{eq} and perform a polynomial regression. A second degree regression was found satisfactory with good correlation coefficients.

Choose a discrete set of values of T_{eq} within the experimental range. Indeed, for a given T_C the T_{eq} value of various molar masses are different. If one wants to compare the Soret coefficients of different molar masses, one needs to select a reference temperature. In fact, a discrete set of reference temperatures was selected.

For each reference temperature calculate s_T by interpolation on the regression curves obtained in step 3. A set of data (M, s_T) is obtained.

For each chosen value of T_{eq} the following regression is carried out, by assuming a power dependence between s_T and M:[23]

$$\ln s_T = \ln c + b \quad \ln M \tag{18}$$

and c and b are determined. Two sets of data (T, c) and (T, b) are created.

The b and c coefficients of the power law of s_T *vs.* M appear to vary with temperature. Therefore, the Soret coefficient can be expressed as:

$$s_T = c(T) \quad M^{b(T)} \tag{19}$$

A regression analysis of b and c *vs.* T is performed according to the following equations:

$$c(T) = c_0 + c_1 \quad T + c_2 \quad T^2 \tag{20}$$

$$b(T) = b_0 + b_1 \quad T + b_2 \quad T^2 \tag{21}$$

Thermodiffusion Coefficient

The thermodiffusion coefficient D_T is the product of the Soret coefficient and the ordinary diffusion coefficient D, which can be calculated by means of the following equation:[24]

$$D = \frac{k \quad T}{6 \quad \pi \quad \eta}\left(\frac{10 \quad \pi \quad N_A}{3 \quad [\eta] \quad M}\right)^{1/3} \tag{22}$$

where k is the Boltzmann's constant, N_A is Avogadro's number and $[\eta]$ is the intrinsic viscosity. This parameter can be calculated by means of the Mark-Houwink relationship:

$$[\eta] = K \quad M^{\beta} \tag{23}$$

In the case of decalin, only Mark-Houwink's coefficients K and β for pure *trans* decalin and for 73% *trans* + 27% *cis* decalin were found in the literature. Anyway, fortunately, at the temperature of 333 K, K and β are identical for those two solvents, and equal to 0.022 cm^3 g^{-1} and 0.63, respectively,[25] and hence, likely identical for any mixture of *cis* and *trans* isomers. So, by applying Eqs. 19, 22, and 23, one can calculate s_T and D, whose product gives D_T, for various molar masses at 333 K, and check whether D_T depends or not on molar mass at that temperature.

EXPERIMENTAL

The experimental apparatus is identical to the one already employed by some of the authors for studies of selectivity in ThFFF in the case of polystyrene in decalin.[11]

The ThFFF system was a Model T-100 Polymer Fractionator (FFFractionation, LLC, Salt Lake City, UT, USA). The coolant liquid, a mixture of water and glycerin, was circulated by means of a Model Haake N3-B Thermostat (Haake Mess-Technik GmbH, Karlsruhe, Germany). Channel dimensions were 45.6 cm tip-to-tip length, 1.9 cm width and 0.0127 cm thick. The void volume at room temperature was calculated from the retention time of an unretained solute (acetone) and resulted to be 1.08 ± 0.04 cm^3 (30 data points): this value agrees with the geometrical value of 1.05 cm^3.

Carrier flow was generated by a Model 420 pump (Kontron Instruments S.p.A., Italy) operating at flow rate values ranging from 0.1 to 0.212 cm^3 min^{-1}. A stop flow time of 1 min was observed for sample relaxation. The carrier was *cis* + *trans* decalin (Fluka Chemie, Buchs, Switzerland) (51% *cis* + 49% *trans*, determined by means of gas chromatographic analysis) at HPLC grade.

The sample was injected through a Model 7725i Rheodyne valve (Rheodyne, Cotati, CA, USA). The injected sample amount is reported in Table 2. The same solvent employed as carrier liquid was used for the sample solutions. Irganox 1010 (Fluka) as antioxidant was added in such batch solutions of the sample at a concentration approximately 10 times lower than the sample. Polymer samples were obtained from Polymer Laboratories Ltd (UK): their specifications are reported in Table 2. Peak molar mass is referred as M_P.

The detector employed was either an UV Model 106 (Linear Instruments Corporation, Reno, NV, USA), operating at 254 nm, or an Evaporative Mass Detector (EMD) Model PL-EMD (Polymer Laboratories Ltd., Church Stretton, Shropshire, UK) operating at 160°C. Nitrogen flow at 2 atm-10 l min^{-1} was used for nebulization. In a previous work[11] these two detectors showed the same accuracy in determination of retention time.

Data handling and ThFFF operations control were driven by TEMP1307 propriety software from FFFractionation LLC (Salt Lake City, UT, USA) running on a cloned 486 computer, which was equipped with an I/O acquisition board Model AT-MIO (National Instruments, Austin, TX, USA).

Table 2

Specifications for the Samples Used

M_p (g mol^{-1})	Polydispersity Polydispersity	Injected Amount (µg)	Evaluation of Retention Time
120,000	1.03	100	From peak baricenter
220,000	1.03	100	From peak baricenter
330,000	1.04	60	From peak baricenter
565,000	1.04	20	From peak baricenter
1,030,000	1.05	20	From peak baricenter

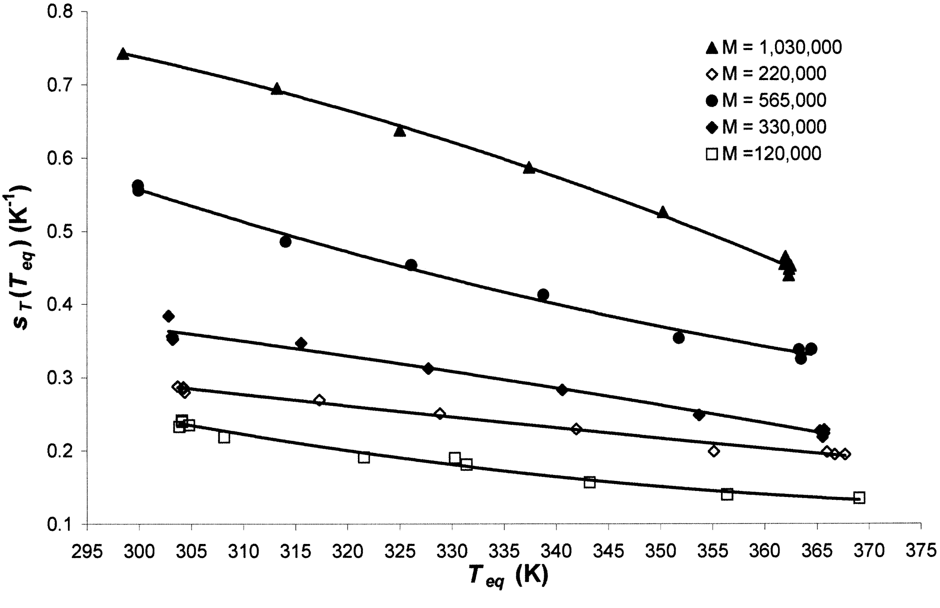

Figure 1. Experimental data of Soret coefficient *vs.* equivalent temperature. The lines correspond to second order polynomial regressions.

Table 3

Coefficients for Equation $s_T = \left(c_0 + c_1T + c_2T^2\right)M^{\left(b_0 + b_1T + b_2T^2\right)}$

	c_0	c_1	c_2	b_0	b_1	b_2
Mean value	1.35 10^{-2}	-7.8 10^{-5}	1.12 10^{-7}	-4.1	2.8 10^{-2}	-4.2 10^{-5}
Error (confidence level 95%)	0.05 10^{-2}	0.3 10^{-5}	0.04 10^{-7}	0.5	0.3 10^{-2}	0.4 10^{-5}
Squared correlation coefficient			0.999			0.988

RESULTS AND DISCUSSION

In Figure 1 the plotted points correspond to all the experimental data collected: *R* values were converted in the corresponding values of equivalent temperature, T_{eq}, and of Soret coefficient, s_T. It must be pointed out that measurements were performed at different values of ΔT, ranging from 19 K to 50 K. In fact, there are experimental indications[14] that the influence of ΔT on T_{eq} is much lower than that of T_C. ΔT was selected in order to satisfy the condition λ_{app}<0.2, for which Eq. 6 is valid.[13] For each molar mass considered in Figure 1, a second order polynomial regression was performed. Then, the 4th thru 7th steps of the procedure described in the Numerical Handling section were executed. The c_i and b_i obtained by this way are reported in Table 3, together with errors and correlation coefficients. It can be seen that all the c_i and b_i coefficients are significantly different from zero. Moreover, the correlation degree is close to unity. By substituting in Eq. 19 the c_i and b_i values reported in Table 3, we obtain the following equation:

$$s_T = (1.35 \quad 10^{-2} - 7.8 \quad 10^{-5} \quad T + 1.12 \quad 10^{-7} \quad T^2) \cdot M^{(-4.1 + 2.8\ 10^{-2}\ T - 4.2\ 10^{-5}\ T^2)} \tag{24}$$

which is also plotted in Figure 2. By means of Eq. 24, a universal calibration for the polystyrene-decalin system is available since a general function of s_T on both *T* and *M* is found. As pointed out by Giddings,[5] such a calibration procedure is truly universal and Eq. 24 can be used in any ThFFF system in the world for the polystyrene-decalin system in the range of experimental parameters here exploited. Within that range, Eq. 24 may be used for exploiting the experimental conditions of fractionation for given values of T_C and ΔT.

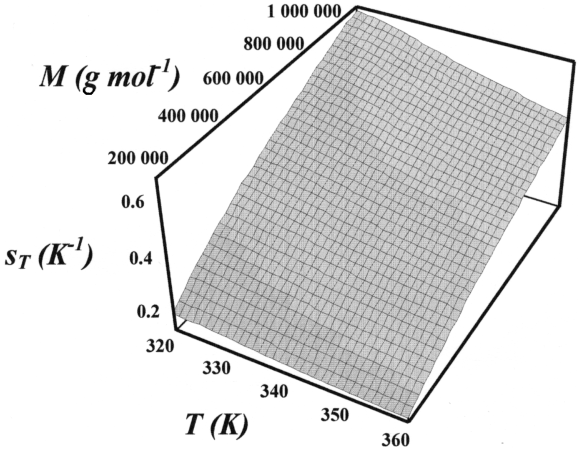

Figure 2. Calculated $s_T(T, M)$ curves (Eq 24. and Table 3)

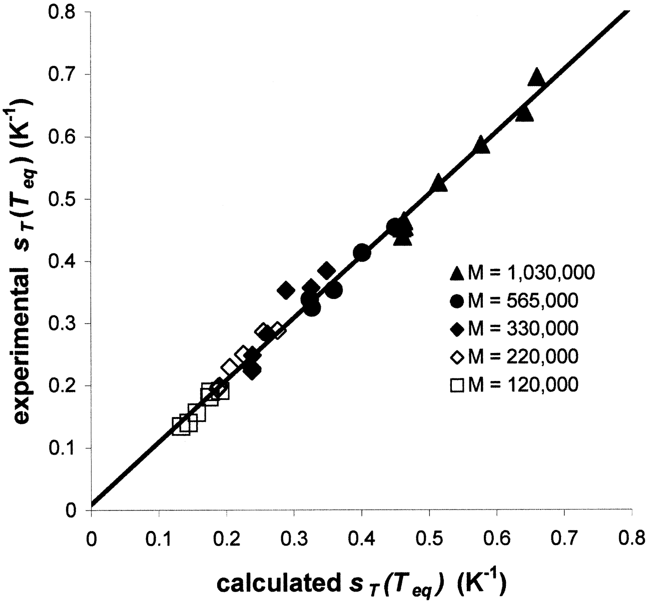

Figure 3. Statistical comparison between experimental values of the Soret coefficient and the corresponding values calculated by using Eq. 24 and Table 3.

The effective goodness of Eq. 24 has been quantified by plotting experimental *vs.* calculated s_T values (see Figure 3) and then by performing a linear regression, which gave the following result:

$$s_{T,\mathrm{exp}} = 0.009\ (\pm\ 0.02) + 1.00\ (\pm\ 0.04)\ s_{T,\mathrm{calc}} \tag{25}$$

$r^2 = 0.986$, 95% confidence level

where r is the correlation coefficient. The fact that in Eq. 25, the intercept is not significantly different from zero and that the slope is not significantly different from unity, with the mean value exactly equal to unity, is the validation of the whole procedure leading to Eq. 24 and Table 3.

Besides the determination of the Soret coefficient illustrated above, a further example of an application of ThFFF for the experimental determination of a physico-chemical parameter, which is very difficult or not practical to be measured by using other techniques, is given here. We show how to determine the thermodiffusion coefficient for polystyrene in *cis* + *trans* decalin at 333 K. At that temperature, the Mark-Houwink coefficients K and β in Eq. 23 for the mixture of *cis* and *trans* decalin used in this work are known from literature.[25] Hence, the calculation of the ordinary diffusion D from Eqs. 22 and 23 is immediate. Then, by using Eq. 24 and Table 3 we can calculate the Soret coefficient at 333 K for all the molar masses here considered. Finally, the thermodiffusion coefficient D_T is, trivially, the product between Soret coefficient and the ordinary diffusion coefficient. Results of this calculation are reported in Table 4. It can be seen that the agreement between D_T and the average value $\langle D_T \rangle$ is within 5%, but a distinct trend is detected from negative to positive values. These data seem to indicate an effective dependence of D_T on M, usually considered to be negligible. Eqs. 22 and 23 show that the exponent of the power law of D *vs.* M is equal to $-(1 + \beta)/3$, which in the present case, is equal to -0.543. This value, combined with that of $b(T)$ at 333K, calculated from Eq. 21 and Table 3 and equal to 0.566, allows one to estimate the exponents of the

Table 4

Dependence of Thermodiffusion Coefficient on Molar Mass at 333K

M (g mol^{-1})	$s_T(333)$ (K^{-1})	D (cm^{2}s^{-1})	$D_T(333)$ (cm^{2}s^{-1}K^{-1})	$\langle D_T(333)\rangle$ (cm^{2}s^{-1}K^{-1})	Difference %	Slope $D_T(M)$ (cm^{2}s^{-1}K^{-1}g^{-1}mol)
120,000	0.172	$1.47\ 10^{-6}$	$2.54\ 10^{-6}$	$2.65\ 10^{-7}$	-4.05	$2.23\ 10^{-14}$
220,000	0.245	$1.06\ 10^{-6}$	$2.60\ 10^{-7}$		-1.78	
330,000	0.311	$8.50\ 10^{-7}$	$2.64\ 10^{-7}$		-0.240	
565,000	0.425	$6.35\ 10^{-7}$	$2.70\ 10^{-7}$		1.85	
1,030,000	0.602	$4.58\ 10^{-7}$	$2.76\ 10^{-7}$		4.23	

power law of D_T *vs.* M to be 0.024. To decide whether this data is significant or not would require a deep chemometric analysis of the whole procedure, which lays beyond the aims of the present work. In any case, to precisely define the effective dependence of D_T on M is relevant, in order to establish both the best analytical conditions of analysis and for physico-chemical studies. All these questions are not the principle aim of this study, but the results of the present approach can be the basis for specific investigations of the topic.

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