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Prediction of Polymer Thermal Diffusion Coefficients from Polymer-Solvent Interaction Parameters: Comparison with Thermal Field Flow Fractionation and Thermal Diffusion Forced Rayleigh Scattering Experiments

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Prediction of Polymer Thermal Diffusion Coefficients from Polymer-Solvent Interaction Parameters: Comparison with Thermal Field Flow Fractionation and Thermal Diffusion Forced Rayleigh Scattering Experiments

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In this study a model that allows the qualitative prediction of polymer thermal diffusion coefficients from polymer-solvent interaction parameters is presented. The Flory-Huggins lattice theory served as a starting point for the thermal diffusion model. From this model it follows that D_T is determined by the temperature dependence of the polymer-solvent interaction parameter (χ), the segmental mobility of the polymer chain, and the polymer concentration. In agreement with literature data, the model predicts that D_T is independent of the molecular mass of the polymer, D_T increases with temperature, and D_T is strongly dependent on the interaction between the polymer and the solvent. Furthermore, it follows from the model that D_T should decrease with concentration. A good qualitative agreement with experimental data has been found. In order to study the potentials of the model, the D_T values of polystyrene (PS) in several solvents were predicted. The required temperature-

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dependent polymer-solvent interaction parameters were calculated from Hildebrand's solubility parameters of the polymer and of the solvent. The solvent's solubility parameters were estimated using Lee and Kesler's generalized thermodynamic equations of state. The polymer solubility parameters were taken from the literature. Lack of data complicated the comparison. However, a good agreement for PS in THF, MEK, dioxane, and cyclohexane was found. Thermal diffusion values predicted for PS in several aromatic solvents were, however, significantly low. Still, the overall result is satisfactory considering the fact that the Flory-Huggins theory is a highly simplified polymer-solvent theory that was never intended to be used for quantitative purposes.

Keywords: Polymer thermal diffusion model; Thermal field-flow fractionation; Polymer-solvent interaction parameter; Thermal diffusion forced Rayleigh scattering

The formation of a concentration gradient in a binary mixture as a result of a temperature gradient is called thermal diffusion. In other words, thermal diffusion is the relative motion of the components of a mixture arising from a temperature gradient. The resulting composition gradients in the mixture lead to normal diffusion, which tends to eliminate the gradients. A steady state is reached when the separating effect of thermal diffusion is balanced by the remixing effect of normal diffusion.

Thermal diffusion may occur in both gaseous and liquid mixtures. A kinetic theory that explains thermal diffusion in gases has been developed by Chapman^[1]. The description of thermal diffusion in liquids, however, turned out to be much more difficult. Although Ludwig already observed the effect in liquids in 1856 and Soret systematically studied it in 1879^[2,3], it is still a poorly understood and relatively unknown phenomenon. The relative obscurity of thermal diffusion may partly be explained by the need for sometimes complicated theories. For example, thermal diffusion can be described by Onsager's theory of nonequilibrium thermodynamics^[2,4-6]. This theory, however, does not give values for thermal diffusion coefficients, not even trends^[7]. Numerical values on thermal diffusion coefficients are needed in the practice of thermal field-flow fractionation analyses for optimization purposes. Frequently, for lack of something better, thermal diffusion is described by phenomenological laws. These laws are phenomenological in the sense that they are experimentally verified but are not part of a comprehensive theory. They describe irreversible processes, such as heat flow in a temperature gradient (Fourier's law) and flow of matter in a concentration gradient

(Fick's law), in the form of proportionalities. The general form of these relationships for a one-dimensional system is^[2,7]

$$J = -A \frac{\partial F}{\partial x} \quad (1)$$

where J is a flux, A is a constant, and F is a potential.

When the aforementioned transport processes occur simultaneously, interference gives rise to cross-phenomena, such as thermal diffusion^[8]. The resulting flux in binary mixtures under non-isothermal conditions can be phenomenologically described by adding an extra term to Fick's law proportional to the temperature gradient (this result also follows from Onsager's theory of irreversible thermodynamics)^[4,9]

$$J = D_T c \frac{\partial T}{\partial x} - D \frac{\partial c}{\partial x} \quad (2)$$

where T is the temperature, c is solute concentration, D is the normal molecular diffusion coefficient, and D_T is the thermal diffusion coefficient. The ratio of D_T over D is the so-called Soret coefficient.

A second reason for the relative obscurity of thermal diffusion is the magnitude of the effect. When we consider the weakness of the force generated by a thermal gradient as compared with the opposed remixing force generated by Brownian motion, i.e., normal diffusion, it is easy to understand that it is often overlooked and neglected. However, in engineering processes involving large molecular mass disparities and large temperature gradients, such as chemical vapor deposition, this can lead to considerable errors^[10]. In recent years liquid thermal diffusion has aroused interest in diverse fields such as the analysis of hydrodynamic instability in mixtures^[11], mass transport in living matter^[12], and migration of minerals^[13].

The thermal diffusion effect has been successfully utilized as a driving force for the separation of a variety of materials^[14], but most of the applications have faded due to the high energy costs of these methods. In general, thermal diffusion can be the predominant force only if the normal diffusion is small enough. This is the case for polymers where the normal diffusion coefficients are approximately 10^{-10} to 10^{-12} m²/s, much smaller than for low-molecular-mass organic liquids.

In the late 1960s Giddings developed a thermal-diffusion-driven polymer separation technique known as thermal field-flow fractionation (ThFFF)^[7]. As a result of this, thermal diffusion has gained more practical importance in recent years.

ThFFF is a separation method especially suited to analyze (high-molecular-mass) polymers, microgels, and particles. The mass working range for polymers is approximately 10^4 – 10^8 Da and for microgels and

particles the size range is about 20 nm–10 μm , making ThFFF a versatile analysis method.

A ThFFF apparatus consists of a flat channel through which a liquid is allowed to flow in a laminar way. A strong temperature gradient (in the order of 1 K/ μm) is created perpendicular to the liquid flow. A small amount of polymer sample is injected in the flow stream and is transported down the channel by the axial flow. At the same time the solute is driven to one of the walls (often the cold wall) by the thermal diffusion effect. Retention and possible fractionation of polymeric constituents depend on the average distance from the wall that a particulate solute zone occupies. This is determined by the Soret coefficient and the temperature gradient according to

$$\frac{t_R}{t_0} \approx \frac{1}{6} \left(\frac{D_T}{D} \right) \Delta T \quad (3)$$

where t_R is the retention time of a particular solute, t_0 is the void time (i.e., residence time of small solvent molecules), and ΔT is the temperature difference between the walls^[15].

Although ThFFF represents a powerful separation technique and has found many applications, its effective use is still somewhat hampered by the poor understanding of the thermal diffusion phenomenon. Because the thermal diffusion effect is not well understood and cannot be predicted, the development of ThFFF separations of new polymers or particles has always been based on a trial-and-error approach. Furthermore, as we cannot yet relate D_T to other physical polymer properties, it remains difficult to correlate retention behavior to polymer or particle characteristics.

A polymer-solvent model that is able to predict polymer thermal diffusion coefficients would greatly aid in the applicability of ThFFF. Several attempts to develop a thermal diffusion theory have been undertaken. Unfortunately, none of these theories could be effectively used to predict D_T values of polymers or could be sufficiently tested owing to lack of experimental data^[16].

In this study we present a new model, based on the Flory-Huggins lattice model for polymer solutions, that enables us to predict, at least qualitatively, thermal diffusion coefficients of polymers from their polymer-solvent interaction parameters. This approach is based on the general knowledge that the polymer-solvent interaction parameter, χ (also known as the Flory-Huggins interaction parameter), is temperature dependent^[17,18]. This is identical to stating that in a temperature gradient the chemical potential is temperature dependent, which in turn leads to a thermal force and accompanying mass flux, which results in thermal diffusion.

Since insufficient data exist today to characterize the temperature dependence $\chi(T)$ of many polymer-solvent systems, in this study we use the well-known relationship between the polymer-solvent χ -parameter and Hildebrand's solubility parameter, δ . For the latter we can estimate the temperature dependence by using earlier developed generalized thermodynamic functions^[19,20]. Thermal diffusion coefficients of polystyrene in a number of solvents are estimated by this method. Preliminary results are discussed and compared with experimental values.

POLYMER THERMAL DIFFUSION

The development of ThFFF has led to a considerable gain in knowledge about polymer thermal diffusion. ThFFF turned out not only to be a unique method to analyze polymers but also to measure polymer D_T values accurately^[21]. In fact, the majority of polymer thermal diffusion data has been measured with ThFFF. Other, often less reliable, methods that were used mainly in the 1950s and 1960s are the moving boundary method^[22], the thermogravitational column^[23], and the static cell method^[24]. Unfortunately, often strongly biased results are obtained by the different methods. Older methods especially show inconsistencies sometimes as high as a factor of two to five. A recently developed method that shows great promise to determine D_T values is thermal diffusion forced Rayleigh scattering (TDFRS). This technique allows the determination of D_T as well as D in one single measurement^[25].

In Table I, an overview of the thermal diffusion values found for polystyrene (PS) in a number of solvents reported in the literature is given. It can be seen that the data show a considerable inconsistency between the different studies and techniques. Therefore, it was decided to consider only the most recent measurements (ThFFF and TDFRS) for comparison between the predicted and experimental D_T values later on in this study. Also, by examining Table I it becomes clear that some of the earliest ThFFF measurements of D_T values are inconsistent with the most recent studies; the D_T values reported by Giddings and coworkers^[21] are systematically high. This is probably due to an inaccurate correction for the solvent viscosity, leading to an erroneous ThFFF retention model.

Even though the quantitative data is inconsistent, within the error limits of presently available data, certain qualitative trends have emerged. There is consensus that D_T is strongly dependent on the composition of the solvent and the polymer^[38]. This feature of D_T has been used to separate polymers of equal molecular mass by their chemical composition^[39].

Most ThFFF studies indicate that the D_T value of polymers is almost independent of the molecular mass^[16,35]. Furthermore, measurements of

TABLE I Overview of experimental D_T values for diluted PS in several solvents

Solvent	D_T (10^{-11} m ² /sK)	T (K)	Method	Year	Ref.
Toluene	0.9–1.05	293	Static cell	1962	24
	0.55–1.6	?	Moving boundary	1961	26
	1.09–1.25	293	Moving boundary	1969	22
	0.9–1.1	?	Moving boundary	1955	27
	1.0–1.05	293	Moving boundary	1963	28
	0.9–1.07	318	Thermograv. column	1964	23
	1.03	295 (T_{cold}) ^a	ThFFF	1989	16
	1.2	295–305	ThFFF	1976	21
	1.05	297	TDFRS	1995	25
	1.10	298	Thermograv. column	1994	29
	MEK	1.7–2.3	293	Moving boundary	1969
1.39		295 (T_{cold})	ThFFF	1989	16
1.9		295–305	ThFFF	1976	21
THF	1.00	295 (T_{cold})	ThFFF	1989	16
	0.92	289–298 (T_{cold})	ThFFF	1995	30
	0.97	299 (T_{cold})	ThFFF	1999	31
	0.94	?	ThFFF	1993	32
	1.15	?	ThFFF	1997	33
Dioxane	0.92	290	ThFFF	1997	34
	0.6	295–305	ThFFF	1976	21
	0.42	296–301 (T_{cold})	ThFFF	1996	35
Ethylbenzene	0.95	295 (T_{cold})	ThFFF	1989	16
	1.19–1.27	303–308	ThFFF	1976	21
	0.94–1.04	289 (T_{cold})	ThFFF	1974	36
Benzene	0.94	295	ThFFF	1985	37
	0.89	295 (T_{cold})	ThFFF	1989	16
Cyclohexane	0.65–0.84	308	Moving boundary	1969	22
	0.66	295 (T_{cold})	ThFFF	1989	16
	0.92	295–305	ThFFF	1976	21

^a T_{cold} is thermal diffusion given at the cold wall temperature of the ThFFF apparatus.

thermal diffusion coefficients of low-molecular-mass organic solvents such as toluene and benzene in thermogravitational columns showed that they were in the same range as for polymers, thereby confirming that D_T is independent of molecular mass^[40].

Experiments have also shown that the geometrical structure of the polymer appears to be of little importance; e.g., linear PS shows the same D_T value as star-shaped PS^[41]. This supports the idea that rather than the molecular architecture of polymers, it is the repetitive segment that determines D_T , as was previously predicted by Khazanovich^[42]. Furthermore, experiments with star-block copolymers have shown that the thermal diffusion is mainly determined by the outer region of the polymer^[43]. This is also the case for particulates (e.g., core-shell lattices^[44,45] and solid silica particles with grafted layers^[46,47]). For random (linear) copolymers, it has been found that the thermal diffusion is the weighted average of the D_T values of the corresponding homopolymers^[32]. Providing that the normal diffusion coefficient is determined by a second technique, this feature can be used to determine the compositional heterogeneity of copolymers by ThFFF^[30,31,33,48].

A few studies have been reported on the temperature behavior of the D_T of polymers. In nearly all studies a clear increase of D_T with temperature was found^[37,49]. As the thermal diffusion differs strongly per solvent, it is conceivable that the temperature dependence of the thermal diffusion also changes with solvent.

Experiments performed by Kirkland and Yau^[50] on a range of polymers in a number of solvents showed that D_T of polar polymers in aqueous solvents is often negligible. It appears, however, that synthetic polymers in organic solvents can also exhibit a negligible thermal diffusion, e.g., polytetrahydrofuran in methyl ethyl keton^[35].

All these results suggest that thermal diffusion is determined mainly by the polymer-solvent interaction and can, therefore, be regarded as a mainly enthalpy-driven process. This reasoning supports our choice of using the Flory-Huggins approach, as in this model the polymer-solvent interaction parameter is supposed to be mainly enthalpic in nature^[17,18,51].

A number of thermal diffusion theories have been developed that vary widely in conceptual basis and success. These include a statistical mechanical theory by Bearman, Kirkwood, and Fixman^[52], a thermal radiation pressure theory by Gaeta^[53], and kinetic theories by Emery and Drickamer^[54], Ham^[55], Khazanovich^[42], and McNab and Meison^[56]. More recently Lhuillier^[57] and Semenov^[58,59] have put forward interesting approaches using surface potentials, osmotic pressures, and hydrodynamic forces for colloidal particles in various solvents, out of the scope of the present study on polymers. The statistical mechanical theory by Bearman, Kirkwood, and Fixman^[52] correlates the Soret coefficient to a heat-transfer term Q . The Soret coefficient is predicted to be independent

of the molecular mass. This is in strong contrast with the experimental data, which shows that D_T rather than D_T/D is mass insensitive. In the thermal radiation pressure theory of Gaeta^[53] (originally developed for hard spheres), the thermal diffusion phenomena are considered to be a consequence of the mechanical interaction of thermal elastic waves and matter. In contrast to all other kinetic models, this theory predicts that macromolecular material can migrate toward either the hot region or the cold region. We will come back to this point later in view of our own prediction. Unfortunately, the model predicts a significant mass or size dependence, again in contrast with the experimental data.

The kinetic collision theory by McNab and Meison^[56] relates the thermal diffusion to the thermal conductivities of the polymer and of the solvent, as well as solvent viscosity and density. Unfortunately, it fails to predict the correct trends. The kinetic theory of Emery and Drickamer^[54] assumes a lattice model not unlike the Flory-Huggins approach. Thermal diffusion is imaged as a process involving a series of activated transitions. The activation energy required for the transfer of a solute from its position to a vacant position in the lattice can be related to the heat of transfer and, by using expressions derived by Tyrrell^[2], to the Soret coefficient. The theory correctly predicts the molecular mass independence of the thermal diffusion, but it completely fails to predict the correct magnitude or even the sign of the thermal diffusion.

Both Ham^[55] and Khazanovich^[42] use an identical approach for their kinetic theories. Their models predict that D_T is independent of the molecular mass and concentration. From the theory developed by Ham it follows that D_T is, at high molecular mass, independent of the polymer composition and depends only on the solvent composition, which is clearly not the case. Khazanovich, on the other hand, by taking into account the segmental mobility of polymer chains, concluded that the thermal diffusion is not only influenced by the nature of the solvent, but also by the segmental diffusion of the polymer beads that make up model pearl-string chains. However, lack of data makes it difficult to fully test this theory. In a recent study by Bender^[60] an attempt was made to estimate the required data, and it appeared that the Khazanovich theory could be successfully used to predict D_T values. However, an in-house validation could not confirm these results. We tested Bender's method for the polymer-solvent systems given by van Asten and coworkers^[35] and found that it was unable to accurately predict the thermal diffusion values. In a recently developed thermal diffusion model by Schimpf and Semenov^[59], D_T is related to the temperature-dependent osmotic pressure gradient in the solvent layer surrounding the monomer units. This is not unlike our own approach via $\chi(T)$ as osmotic pressures are directly related to chemical potentials^[59,61]. The model appears to be in qualitative agreement with some experimental data. It correctly predicts a very low D_T value for polymers in water, but predicts a negligible D_T in

toluene as well, which strongly contradicts with experimental literature data^[59].

An extensive overview and evaluation of most of the above-mentioned theories is given by Schimpf and Giddings^[16]. As none of the existing theories could be used to satisfactorily predict D_T , Schimpf and Giddings also made an effort to relate the thermal diffusion to polymer and solvent physical properties by using regression methods. They succeeded in finding a relation between D_T and thermal conductivity of the polymer and of the solvent and the activation energy for the viscous flow of the solvent. However, this correlation could not be confirmed for other polymer-solvent systems^[35]. Not surprisingly, in several other studies a correlation between thermal diffusion and solubility parameters was found^[2,62]. This correlation was found for polymers as well as for low-molecular-mass liquids but, at the time, did not allow estimating the thermal diffusion.

POLYMER THERMAL DIFFUSION MODEL

In this study it is assumed that the diluted polymer solution can be regarded as a total free-draining pearl-string-like polymer system according to the often-used Flory-Huggins lattice model. Although this model is highly simplified, it explains correctly (at least qualitatively) a large number of experimental observations^[51].

According to the Flory-Huggins theory, the change in the Gibbs function of a polymer-solvent system due to the process of mixing can be described by

$$\Delta G_{\text{mix}} = RT(n_1 \ln \varphi_1 + n_2 \ln \varphi_2 + n_1 \varphi_2 \chi) \quad (4)$$

where R is the universal gas constant, χ is the polymer-solvent (Flory-Huggins) interaction parameter, φ_1 is the solvent volume fraction, φ_2 is the polymer volume fraction, and n_1 and n_2 are the number of moles of the solvent and the polymer, respectively^[51].

As, from the above, it may be assumed that thermal diffusion is determined mainly by enthalpic interactions, the entropic part of the Flory-Huggins equation, or the first two terms of the right-hand side of Equation (4) can be neglected.

The enthalpy of mixing ΔH_{mix} can now be derived by applying the standard thermodynamic relation $\Delta H_{\text{mix}} = -T^2[\partial(\Delta G_{\text{mix}}/T)/\partial T]$. The corresponding chemical potential $\Delta \mu_2^H$ of a polymer in a solvent can then be calculated from the enthalpy of mixing

$$\Delta \mu_2^H = \frac{\partial \Delta H_{\text{mix}}}{\partial n_2} = -RT^2 \left(\frac{\partial \chi}{\partial T} \right) \varphi_1^2 \frac{V_2}{V_1} \quad (5)$$

where V_1 and V_2 are the molar volumes of the solvent and the polymer, respectively. We have to note that, formally, the chemical potential is defined at a constant temperature. However, in order to stay within the framework of equilibrium thermodynamics, we relax this requirement, realizing that the temperature differences applied are relatively small and amount to only 10–20% of the absolute temperature. Knowing the chemical potential difference from Equation (5), we are now in a position to calculate the accompanying force, being the gradient in the potential.

The resulting force per molecule in a temperature gradient is then given as:

$$F = -\frac{\partial \Delta \mu_2^H}{N_A \partial x} = k \varphi_1^2 \frac{V_2}{V_1} \frac{\partial \left[T^2 \left(\frac{\partial \chi}{\partial T} \right) \right]}{\partial T} \frac{\partial T}{\partial x} \quad (6)$$

where k is Boltzmann's constant and N_A is Avogadro's number. The corresponding flux generated by this thermal force is $J = c \cdot v$ where v is the linear displacement velocity. The latter is found from $v = F/f$, where f is the Stokes-Einstein friction factor. Hence, the flux reads $J = c \cdot F/f$ and, according to the previously mentioned phenomenological laws, can also be written as

$$J = D_T c \frac{\partial T}{\partial x} \quad (7)$$

Combining Equations (6) and (7) leads to the following expression for the thermal diffusion coefficient

$$D_T = k \varphi_1^2 \frac{V_2}{V_1} \frac{1}{f} \frac{\partial \left[T^2 \left(\frac{\partial \chi}{\partial T} \right) \right]}{\partial T} \quad (8)$$

As the Flory-Huggins theory assumes a total free-draining pearl-string-like system, the friction factor in the framework of FH is then determined by the sum of the friction of all segments (N_{seg})

$$f = N_{\text{seg}} f_{\text{seg}} \quad (9)$$

where f_{seg} is the friction factor of one segment. The number of segments in the Flory-Huggins model is equal to V_2/V_1 and therefore,

$$f = \frac{V_2}{V_1} f_{\text{seg}} \quad (10)$$

Combining Equations (8) and (10) leads after some rearranging to the following expression for the thermal diffusion coefficient:

$$D_T = \phi_1^2 \frac{D_{\text{seg}}}{T} \frac{\partial \left[T^2 \left(\frac{\partial \chi}{\partial T} \right) \right]}{\partial T} \quad (11)$$

where D_{seg} is the segment diffusion coefficient, kT/f_{seg} .

Three terms can be distinguished in Equation (11): a concentration-, a diffusion-, and a polymer-solvent interaction term. For highly diluted polymer samples, the thermal diffusion depends only on the segmental mobility of the polymer and on the temperature dependence of the polymer-solvent interaction parameter. This result compares favorably with that of Khazanovich^[42], who also found the proportionality with D_{seg} but a much more complicated energy function. Brochard-Wyart^[5], on the basis of Onsager's irreversible thermodynamics, predicts that D_T is independent of molecular mass also, just as Khazanovich's and our present results. However, numerical results cannot be obtained from that method, in contrast to ours.

As the polymer-solvent interaction parameter is virtually independent of the molecular mass^[63,64], it can be concluded that the predicted thermal diffusion coefficient is, in accordance with experimental data, also independent of molecular mass^[16,35].

Depending on the temperature behavior of the polymer-solvent interaction parameter, the thermal diffusion can, according to Equation (11), have a positive or negative sign. This means that polymers could migrate to the cold wall as well as to the hot wall. Up to now experimental results suggest that polymers migrate largely to colder regions^[65,66]. However, studies of thermal diffusion of low-molecular-mass compounds have shown that compounds can indeed migrate to the hot wall^[2].

From Equation (11) it also follows that D_T can have a value of zero in the case that $\chi/T = \text{constant}$. We note in passing that in the formal Flory-Huggins model $\partial \chi / \partial T = -\chi/T$ if all entropic contributions are neglected^[17]. Thus for that case

$$\frac{\partial}{\partial T} \left[T^2 \frac{\partial \chi}{\partial T} \right] = 0 \quad (12)$$

which consequently yields that $D_T = 0$, always. The experimental fact that D_T is often small but nonzero is another failure for the classical Flory-Huggins theory.

Although the Flory-Huggins model for χ was originally intended only to describe contact enthalpy differences in the lattice, there is no formal objection to include differences in free volume^[18] or alternatively entropic contributions^[17] to χ . Thus it is generally accepted that the χ -parameter is to be divided into two contributions^[63]:

$$\chi = \chi_H + \chi_S \quad (13)$$

where χ_H is the enthalpic contribution given by $-T(\partial\chi/\partial T)$ and χ_S is the entropic contribution given by $\partial(T\chi)/\partial T$. Although not much data is available for $\chi(T)$, the reported data is sometimes to be described by a relationship as

$$\chi = a + \frac{b}{T} \quad (14)$$

where a and b are temperature independent. It is seen that a and b can be identified as $a = \chi_S$ and $b = T\chi_H$. Typical values for χ_S are about 0.3^[17,63,67], while χ_H (see below), can be estimated by the use of solubility parameters. Because $\chi_S = a$ is independent of temperature, χ in Equation (11) can be replaced by χ_H , and we note that D_T should indeed be independent of entropic contributions.

Prediction of the concentration dependence of the thermal diffusion is not straightforward, as the concentration dependence of $\partial\chi/\partial T$ is not known. It follows from theory that the absolute value of χ should increase slightly with polymer concentration^[51]. This slight increase probably has a minor, if any, effect on the temperature dependence of χ and is negligible compared to the influence of φ_1 on the thermal diffusion. By neglecting the possible concentration dependence of $\partial\chi/\partial T$ it follows from Equation (11) that D_T decreases with the polymer volume fraction (as $\varphi_1 = 1 - \varphi_2$). Unfortunately, this effect cannot be verified with ThFFF, because at higher concentrations overloading phenomena easily disturb the analysis. However, in a number of mainly early thermal diffusion studies carried out with other techniques a clear decrease in D_T with concentration was found^[24,27-29,68]. Recent TDFRS measurements showed contrasting results; in one of the first TDFRS studies by Köhler et al.^[25] an almost constant D_T value over a broad concentration range was found, whereas in another study from the same authors a clear decrease in D_T with concentration was found^[69]. The matter is clearly unresolved and requires further study.

PREDICTION OF THERMAL DIFFUSION AND COMPARISON WITH EXPERIMENTAL DATA

In the previous section it has been shown that Equation (11) is in qualitative agreement with experimental observations. In order to test the model more quantitatively, thermal diffusion coefficients for polystyrene in a number of solvents were predicted from Equation (11) and compared with experimental data.

To actually calculate the thermal diffusion coefficient of a polymer via Equation (11), the polymer-solvent interaction parameter needs to be

known at a number of temperatures. Unfortunately, no such data is available in the literature. For that reason, the interaction parameter χ_H was estimated from the well-known Hildebrand's solubility parameters according to^[63,67]

$$\chi_H = \frac{V_m(\delta_s - \delta_p)^2}{RT} \quad (15)$$

where V_m is the molar volume of the solvent, δ is the solubility parameter, and the subscripts s and p refer to the solvent and the polymer, respectively. We have to note that with this simplified model, Hildebrand parameters cannot predict negative values of χ_H .

The solubility parameter of the solvent can be calculated using generalized thermodynamic functions, at a wide range of temperatures and pressures, with^[19,70]

$$\delta_s^2 = -\frac{RT_c}{V} \left[\frac{h - h^0}{RT_c} - T_R(Z - 1) \right] \quad (16)$$

where the reduced temperature T_R is equal to the ratio of the actual temperature and the critical temperature T_c . The values of the enthalpy departure function $(h - h^0)/RT_c$ and the compressibility factor Z are estimated from Lee and Kesler's generalized thermodynamic equations of state^[71]. With this method Tijssen^[72] found for a number of solvents with strongly varying polarities that the total solubility parameter relates to temperature as $\delta^2 = AT + B$. For obtaining these results the molar volume V_m was also estimated by the method of generalized thermodynamic functions. Regression analysis of experimental data on relative volatilities by Barton et al.^[73], resulted in a linear relation, $\delta = CT + D$, between the temperature and the solubility parameter. These results are supported by experimental data from Shen and Lee^[74], who also found an approximate linear relation for a number of solvents. The calculations in the present study are based on Tijssen's method. However, we obtained the molar volumes by the Thomson method^[20] for compressed liquids as this method gives generally better results. The calculated solubility parameters of the solvents listed in Table I are, together with their first derivatives, given in Table II. It was found that the solubility parameters showed an approximately linear behavior over the relatively small temperature range studied (Figure 1).

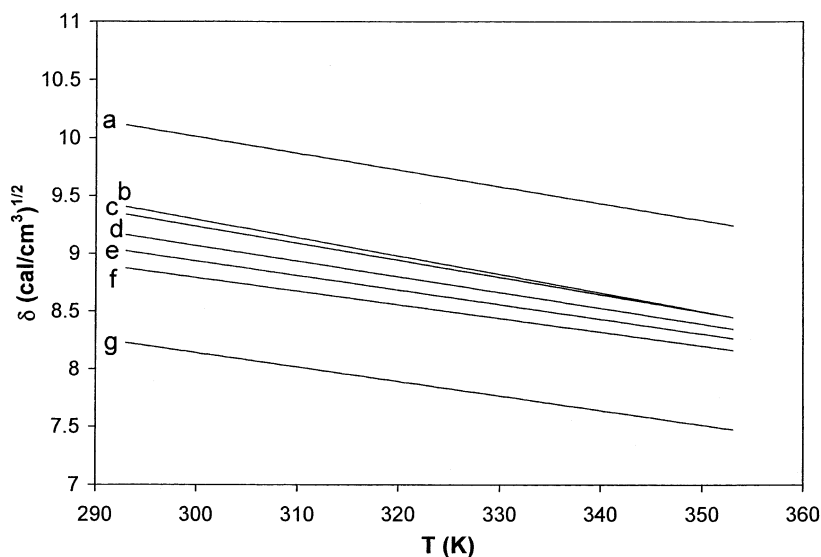
Estimation of the solubility parameter for polystyrene was done from literature data^[63]. Although equations of state for polymer systems have been developed^[18,51,75], they do not allow an accurate estimate of polymer solubility parameters as a function of temperature.

TABLE II Solvent solubility parameters ($T=297\text{ K}$, $P=2\text{ bar}$) and their temperature dependence (293 to 353 K)

Solvent	$\delta_{T=297\text{ K}; P=2\text{ bar}}$ [(cal/cm ³) ^{1/2}]	$\partial\delta/\partial T$ [(cal/cm ³) ^{1/2} /K]
Toluene	8.97	-0.0127
MEK	9.49	-0.0160
THF	9.28	-0.0149
Dioxane	10.05	-0.0145
Ethylbenzene	8.82	-0.0119
Benzene	9.11	-0.0136
Cyclohexane	8.18	-0.0125

From the literature data, we found that the temperature dependence of the solubility parameter of PS also showed an approximately linear behavior, and could, in the temperature range of 293–353 K, be described by^[63]

$$\delta(T) = -7.27 \times 10^{-3}T + 11.22 \quad (17)$$

**FIGURE 1** Solubility parameter as function of temperature. (a) dioxane; (b) MEK; (c) THF; (d) benzene; (e) toluene; (f) ethylbenzene; (g) cyclohexane. The values were calculated from Equation (16).

where δ is commonly expressed in $(\text{cal}/\text{cm}^3)^{1/2}$. In Figure 2 the polymer-solvent interaction parameters of polystyrene in the solvents listed in Table I are plotted as a function of temperature. From Figure 2 it becomes clear that the temperature dependence of the polymer-solvent interaction parameter depends strongly on the type of solvent, and, in most cases, cannot be approximated by Equation (14). Incidentally, the latter was also not expected as substitution of the data given in Table II and Equation (17) into Equation (15) leads to a rather complicated third-order polynomial that strongly depends on the individual values of δ_s and δ_p as well as on the temperature behavior of the molar volume of the solvent. In Table III χ_H , $\partial\chi_H/\partial T$ and $\partial^2\chi_H/\partial T^2$ are given. The temperatures correspond to the temperature at which the experimental D_T values were determined. The χ_H values found for the studied PS-solvent systems show considerable differences in magnitude as well as in sign. Comparison with literature data is difficult, as the available data is not consistent and for the same solvent sometimes shows a very large spread (up to a factor of five)^[63].

The segmental diffusion D_{seg} in Equation (11) was calculated from the segmental radius of a bead in the pearl-string model by using the Stokes-Einstein equation^[8]. The segmental radius for polystyrene of 0.201 nm was taken from the literature^[60]. The predicted thermal diffusion coefficients for PS in several solvents as a function of temperature are, together with experimental values calculated from Table I, given in Table IV. A fair agreement is seen between the predicted thermal diffusion values for PS in THF, MEK, dioxane, and cyclohexane and the experimental values. The thermal diffusion values of PS in the aromatic solvents (benzene, toluene, and ethylbenzene) appear to be systematically low (<45%). We cannot explain these deviations at this moment. The results are, however, quite acceptable considering the large spread in the experimental values and the fact that the present thermal diffusion method is based on a highly simplified polymer-solvent model with many approximations that was never intended for quantitative purposes. For a more accurate quantitative estimate of the thermal diffusion coefficients, a more sophisticated polymer-solvent theory is required, such as the excluded-volume theory, which is applicable at low polymer concentrations, or the Prigogine-Flory equation-of-state theory^[51,75]. Furthermore, instead of using the well-established Hildebrand solubility parameters to calculate χ_H data, it might be worthwhile to study the use of cohesion parameter theories that divide the total cohesion energy into two or more parts, e.g., dispersion-, polar-, and hydrogen bonding-interactions^[63]. The use of the multicomponent interaction parameter theory formulated by Keller et al. would be especially interesting because this theory also allows the prediction of negative values of χ_H ^[76]. Investigation of the influence of entropic effects is another task for future study.

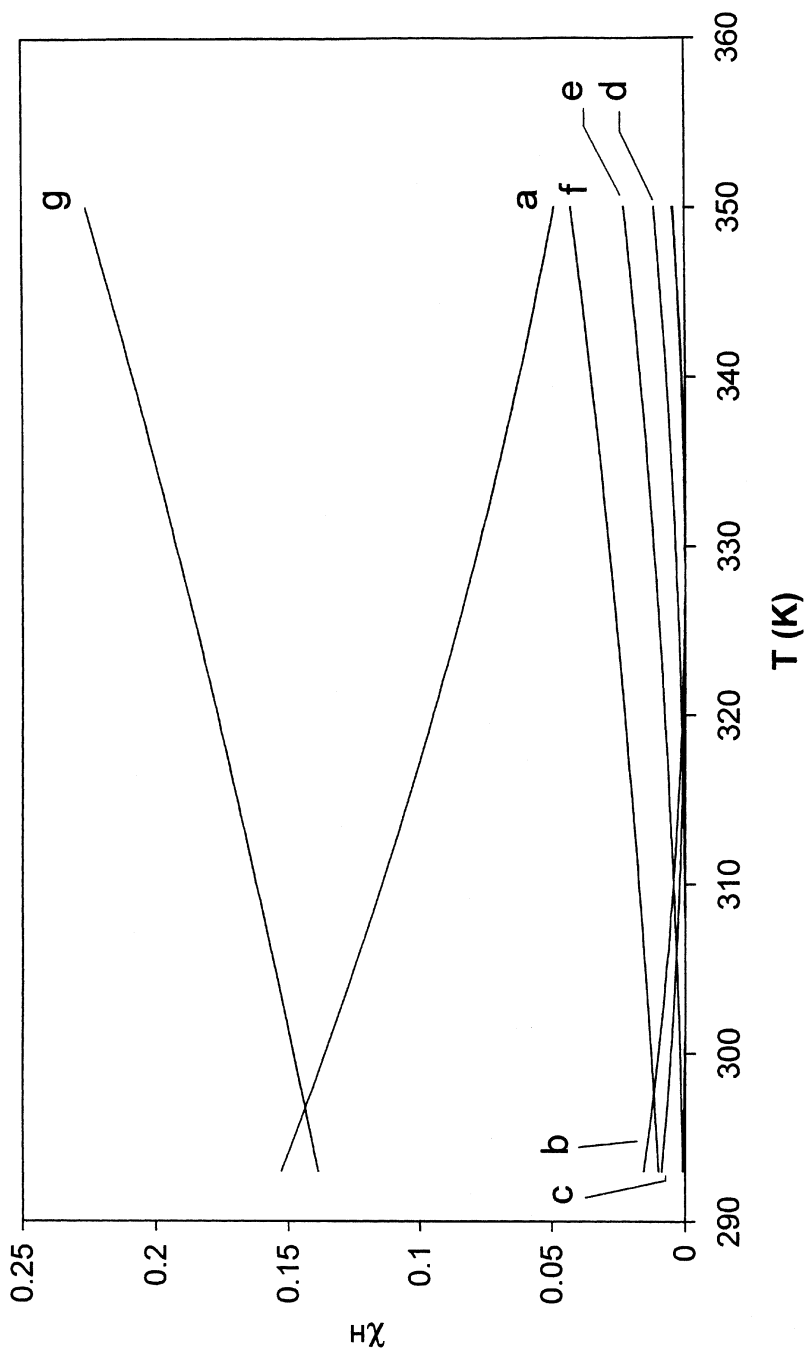


FIGURE 2 Polymer-solvent interaction parameter as function of temperature. (a) PS-dioxane; (b) PS-MEK; (c) PS-THF; (d) PS-benzene; (e) PS-toluene; (f) PS-cyclohexane; (g) PS-ethylbenzene. The values were calculated from Equations (15) and (16).

TABLE III Polymer-solvent interaction parameter data of several PS-solvent systems

Solvent	χ_H (10^{-3})	$\partial\chi_H/\partial T$ (10^{-4}K)	$\partial^2\chi_H/\partial T^2$ (10^{-6}K^2)	T (K)
THF	8.11	-5.08	16.3	294
MEK	13.7	-8.03	24.1	295
Dioxane	145	-23.7	23.8	296
Cyclohexane	141	13.3	6.37	295
Benzene	0.45	-1.02	11.6	295
Ethylbenzene	11.1	3.96	7.11	296
Toluene	1.24	1.54	9.27	296

The predicted thermal diffusion was found to increase with temperature in all solvents. This is in correspondence with literature data, although the experimental data show that the increase in D_T with temperature is often less pronounced^[21,36,37]. This is illustrated in Figure 3 where the predicted D_T of PS in ethylbenzene from Equation (11) (solid line) and the experimental values taken from Brimhall et al.^[37] and van Batten et al.^[49] are depicted.

TABLE IV Predicted and experimental thermal diffusion values of PS in several solvents

Solvent	Predicted D_T ($10^{-11}\text{m}^2/\text{sK}$)	Experimental D_T^a ($10^{-11}\text{m}^2/\text{sK}$)	T (K)
THF	0.86	0.95	294
MEK	1.42	1.39	295
Dioxane	0.54	0.42	296
Cyclohexane	0.52	0.66	295
Benzene	0.56	0.89	295
Ethylbenzene	0.49	0.95	296
Toluene	0.57	1.04	296

^aAverage experimental thermal diffusion coefficients were calculated from the literature listed in Table I. In view of the spread and uncertainty of the data, only the most recent ThFFF and TDFRS studies were considered. Data from Giddings et al.^[21] was excluded because in this study the reported D_T numbers are questionable due to the use of an inaccurate retention model. Furthermore, other ThFFF studies^[32,33] were not taken into account because no measurement temperature was given.

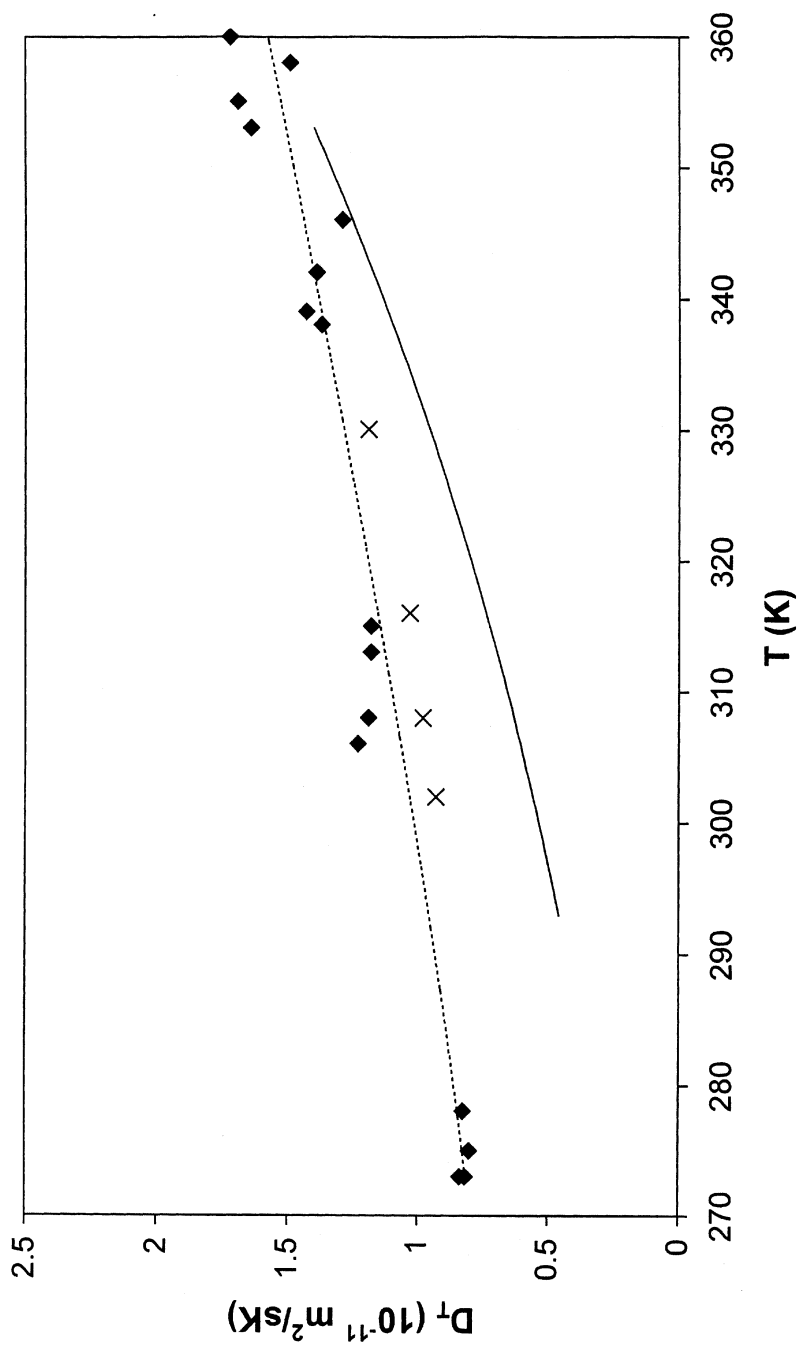


FIGURE 3 Temperature dependence of D_T of PS in ethylbenzene: (—) predicted; (\blacklozenge) experimental values taken from Brimhall et al.^[37]; (\times) experimental values taken from van Batten et al.^[49]; dotted line is the regression curve.

CONCLUSION

In this study it has been shown that polymer thermal diffusion coefficients can be calculated from the Flory-Huggins polymer-solvent interaction parameters. Based on the Flory-Huggins lattice theory a method has been developed that gives a qualitative agreement between the predicted D_T values and the experimental data. Furthermore, considering the many oversimplifications and approximations of the theory, the quantitative prediction of the polymer thermal diffusion coefficient is also reasonably correct. However, the simplicity of the theory in combination with the fact that it has been developed only for moderately concentrated polymer solutions clearly necessitates the use of a more realistic polymer-solvent model for a more accurate prediction of the polymer thermal diffusion coefficient. Furthermore, the influence of entropic effects, although likely to be small, needs to be studied.

REFERENCES

- [1] Chapman, S. and Cowling, T. G. (1939). *The Mathematical Theory of Nonuniform Gases*, Cambridge University Press, Cambridge.
- [2] Tyrrell, H. J. V. (1961). *Diffusion and Heat Flow in Liquids*, Butterworths, London.
- [3] Sanfeld, A. (1971). In *Physical Chemistry, an Advanced Treatise*, 1: *Thermodynamics*, H. Eyring, D. Henderson, and W. Jost, eds., Academic Press, New York, ch. 2.
- [4] de Groot, S. R. (1951). *Thermodynamics of Irreversible Processes*, North-Holland, Amsterdam, ch. 1.
- [5] Brochard-Wyart, F. (1983). *Macromolecules*, **16**, 149.
- [6] Kuiken, G. D. C. (1994). *Thermodynamics of Irreversible Processes, Application to Diffusion and Rheology*, John Wiley, Chichester, UK.
- [7] Giddings, J. C. (1991). *Unified Separation Science*, Wiley-Interscience, New York.
- [8] Bird, R. B., Stewart, W. E., and Lightfoot, E. N. (1960). *Transport Phenomena*, John Wiley, New York.
- [9] Landau, L. D. and Lifshitz, E. M. (1987). *Fluid Mechanics*, Courses of Theoretical Physics, vol. 6, Pergamon Press, Oxford, 230–237.
- [10] Rosner, D. E. (1980). *Phys. Chem. Hydrodyn.*, **1**, 159.
- [11] Platten, J. K. and Legros, J. C. (1984). *Convection in Liquids*, Springer, Berlin.
- [12] Bonner, F. J. and Sundelöf, L. O. (1984). *Z. Naturf.*, **C 39**, 656.
- [13] Costeséque, P. (1985). *Bull. Soc. Fr. Minéral Cristallogr.*, **108**, 305.
- [14] Grodzka, P. G. and Facemire, B. (1977). *Sep. Sci.*, **12**, 103.
- [15] Schimpf, M. E. (2000). In *Field-Flow Fractionation Handbook*, M. E. Schimpf, K. Caldwell, and J. C. Giddings, eds., John Wiley, New York, ch. 16.
- [16] Schimpf, M. E. and Giddings, J. C. (1989). *J. Polym. Sci., Part B: Polym. Phys.*, **27**, 1317.
- [17] Young, R. J. and Lovell, P. A. (1999). *Introduction to Polymers*, 2nd ed., Chapman & Hall, London.
- [18] Fler, G. J., Cohen Stuart, M. A., Scheutjens, J. M. H. M., Cosgrove, T., and Vincent, B. (1993). *Polymers at Interfaces*, Chapman & Hall, London.

- [19] Tijssen, R., Billiet, H. A. H., and Schoenmakers, P. J. (1976). *J. Chromatogr.*, **122**, 185.
- [20] Reid, R. C., Prausnitz, J. M., and Poling, B. E. (1987). *The Properties of Gases and Liquids*, 4th ed., McGraw-Hill, New York.
- [21] Giddings, J. C., Caldwell, K. D., and Myers, M. N. (1976). *Macromolecules*, **9**, 106.
- [22] Meyerhoff, G. and Rauch, B. (1969). *Makromol. Chem.*, **127**, 214.
- [23] Taylor, D. L. (1964). *J. Polym. Sci. A: Polym. Chem.*, **2**, 611.
- [24] Meyerhoff, G. and Nachtigall, K. (1962). *J. Polym. Sci.*, **57**, 227.
- [25] Köhler, W., Rosenauer, C., and Rossmanith, P. (1995). *Int. J. Thermophys.*, **16**, 11.
- [26] Herren, C. L. and Ham, J. S. (1961). *J. Chem. Phys.*, **35**, 1479.
- [27] Hoffman, J. D. and Zimm, B. H. (1955). *J. Polym. Sci.*, **15**, 405.
- [28] Rauch, B. and Meyerhoff, G. (1963). *J. Phys. Chem.*, **67**, 946.
- [29] Ecenarro, O., Madariaga, J. A., Navarro, J. L., Santamaria, C. M., Carrión, J. A., and Saviron, J. M. (1994). *Macromolecules*, **27**, 4968.
- [30] van Asten, A. C., van Dam, R. J., Kok, W. Th., Tijssen, R., and Poppe, H. (1995). *J. Chromatogr. A*, **703**, 245.
- [31] Mes, E. P. C., Tijssen, R., and Kok, W. Th. (1999). *Chromatographia*, **50**, 45.
- [32] Schimpf, M. E., Wheeler, L. M., and Romeo, P. F. (1993). In *Chromatography of Polymers*, T. Provder, ed., ACS Symp. Ser., vol. 521, American Chemical Society, Washington, DC, ch. 5.
- [33] Venema, E., de Leeuw, P., Kraak, J. C., Poppe, H., and Tijssen, R. (1997). *J. Chromatogr. A*, **765**, 135.
- [34] Myers, M. N., Cao, W., Chen, C.-I., Kumar, V., and Giddings, J. C. (1997). *J. Liq. Chromatogr.*, **20**, 2757.
- [35] van Asten, A. C., Kok, W. Th., Tijssen, R., and Poppe, H. (1996). *J. Polym. Sci., Part B: Polym. Phys.*, **34**, 297.
- [36] Myers, M. N., Caldwell, K. D., and Giddings, J. C. (1974). *Sep. Sci.*, **9**, 47.
- [37] Brimhall, S. L., Myers, M. N., Caldwell, K. D., and Giddings, J. C. (1985). *J. Polym. Sci., Part B: Polym. Phys.*, **23**, 2443.
- [38] van Asten, A. C., Kok, W. Th., Tijssen, R., and Poppe, H. (1996). *J. Polym. Sci., Part B: Polym. Phys.*, **34**, 283.
- [39] van Asten, A. C., Stegeman, G., Kok, W. Th., Tijssen, R., and Poppe, H. (1994). *Anal. Chem.*, **66**, 3073.
- [40] Ecenarro, A. O., Madariaga, J. A., Navarro, J., Santamaria, C. M., Carrión, J. A., and Saviron, J. M. (1990). *J. Phys., Condens. Matter*, **2**, 2289.
- [41] Schimpf, M. E., and Giddings, J. C. (1987). *Macromolecules*, **20**, 1561.
- [42] Khazanovich, T. N. (1967). *J. Polym. Sci., Part C*, **16**, 2463.
- [43] Schimpf, M. E. and Giddings, J. C. (1990). *J. Polym. Sci., Part B: Polym. Phys.*, **28**, 2673.
- [44] Ratanathanawongs, S. K., Shiundu, P. M., and Giddings, J. C. (1995). *Colloids Surf. A*, **105**, 243.
- [45] Shiundu, P. M. and Giddings, J. C. (1995). *J. Chromatogr. A*, **715**, 117.
- [46] Venema, E. (1995). Unpublished results.
- [47] Jeon, S. J., Schimpf, M. E., and Nyborg, A. (1997). *Anal. Chem.*, **69**, 3442.
- [48] Jeon, S. J. and Lee, D. W. (1995). *J. Polym. Sci., Part B: Polym. Phys.*, **33**, 411.
- [49] van Batten, C., Hoyos, M., and Martin, M. (1999). *Entropie*, **217**, 61.
- [50] Kirkland, J. J. and Yau, W. W. (1986). *J. Chromatogr.*, **353**, 95.
- [51] Munk, P. (1989). *Introduction to Macromolecular Science*, John Wiley, New York.
- [52] Bearman, R. J., Kirkwood, J. G., and Fixman, M. (1958). *Adv. Chem. Phys.*, **1**, 1.

- [53] Gaeta, F. S. (1969). *Phys. Rev.*, **182**, 289.
- [54] Emery, Jr., A. H. and Drickamer, H. G. (1955). *J. Chem. Phys.*, **23**, 2252.
- [55] Ham, J. S. (1960). *J. Appl. Phys.*, **31**, 1853.
- [56] McNab, G. S. and Meisen, A. (1973). *J. Colloid Interface Sci.*, **44**, 339.
- [57] Lhuillier, D. (1998). *Entropie*, **214**, 23.
- [58] Giddings, J. C., Shiundu, P., and Semenov, S. N. (1995). *J. Colloid Interf. Sci.*, **176**, 454.
- [59] Schimpf, M. E. and Semenov, S. N. (1999). Poster presented at the Eighth International Symposium on Field-Flow Fractionation, Paris.
- [60] Bender, M. (1995). *Macromolecules*, **28**, 1309.
- [61] Orwoll, R. A. (1977). *Rubber Chem. Technol.*, **50**, 451.
- [62] Schimpf, M. E. and Giddings, J. C. (1986). *Polym. Prep.*, **27**, 158.
- [63] *CRC Handbook of Polymer-Liquid Interaction Parameters and Solubility Parameters*. (1990). A. F. M. Barton, ed., CRC Press, Boca Raton, FL.
- [64] Rudolf, B., Schneider, H. A., and Cantow, H.-J. (1995). *Polym. Bull.*, **34**, 109.
- [65] Giddings, J. C., Martin, M., and Myers, M. N. (1979). *Sep. Sci. Technol.*, **14**, 611.
- [66] Martin, M. and Reynaud, R. (1980). *Anal. Chem.*, **52**, 2293.
- [67] *Polymer Handbook*, 3rd ed. (1989). J. Brandrup and E. H. Immergut, eds., John Wiley, New York.
- [68] Whitmore, F. (1960). *J. Appl. Phys.*, **31**, 1858.
- [69] Rossmannith, P. and Köhler, W. (1996). *Macromolecules*, **29**, 3203.
- [70] Tijssen, R., Schoenmakers, P. J., Böhmer, M. R., Koopal, L. K., and Billiet, H. A. H. (1993). *J. Chromatogr. A*, **656**, 135.
- [71] Lee, B. I. and Kesler, M. G. (1975). *AIChE J.*, **21**, 510.
- [72] Tijssen, R. (1976). Unpublished results.
- [73] Barton, P., Holland, R. E., and McCormick, R. H. (1974). *Ind. Eng. Chem., Proc. Des. Dev.*, **13**, 378.
- [74] Shen, Y. and Lee, M. (1998). In *Advances in Chromatography*, vol. 38, J. C. Giddings and R. A. Keller, eds., Marcel Dekker, New York, 106–108.
- [75] Billmeyer, F. W. (1984). *Textbook of Polymer Science*, John Wiley, New York.
- [76] Karger, B. L., Snyder, L. R., and Eon, C. (1978). *Anal. Chem.*, **50**, 2126.