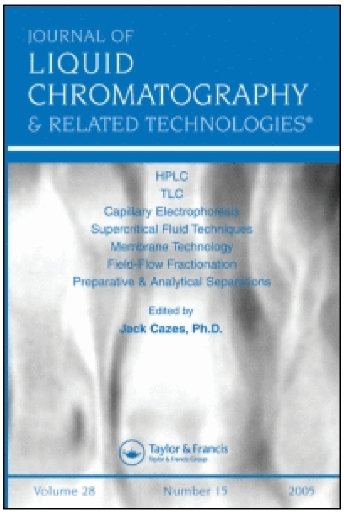

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Effect of Channel Orientation on Thermal Diffusion and Polymer Retention in Thermal Field-Flow Fractionation

Jun Xu[a]; Chad A. Rue[a]; Martin E. Schimpf[a]
[a] Department of Chemistry, Boise State University Boise, Idaho

To cite this Article Xu, Jun , Rue, Chad A. and Schimpf, Martin E.(1997) 'Effect of Channel Orientation on Thermal Diffusion and Polymer Retention in Thermal Field-Flow Fractionation', Journal of Liquid Chromatography & Related Technologies, 20: 16, 2703 — 2722

To link to this Article: DOI: 10.1080/10826079708005588

URL: http://dx.doi.org/10.1080/10826079708005588

J. LIQ. CHROM. & REL. TECHNOL., 20(16 & 17), 2703–2722 (1997)

EFFECT OF CHANNEL ORIENTATION ON THERMAL DIFFUSION AND POLYMER RETENTION IN THERMAL FIELD-FLOW FRACTIONATION

Jun Xu, Chad A. Rue, Martin E. Schimpf*

Department of Chemistry
Boise State University
Boise, Idaho 83725

ABSTRACT

The ThFFF retention of polymers is enhanced in certain liquid mixtures. Previous studies of thermal diffusion in such mixtures indicate that the enhancement is due to an additional solubility-based force induced by a solvent gradient in the channel. The partitioning of solvent mixtures in a temperature gradient was shown to be correlated to solvent density, just as the thermal diffusion of polymers is correlated to polymer density.

This work examines the density effect more closely by looking at the effect of channel orientation on both polymer retention and the partitioning of liquids. A difference in the profiles of solvent partitioning with channel orientation indicates the presence of convection currents in an inverted ThFFF channel, yet polymer retention is independent of channel orientation in homogeneous solvents as well as solvent mixtures. The results indicate that the effect of density on polymer retention is rooted in thermal diffusion and not convection, but that either the previously proposed mechanism of enhanced retention is incorrect or convection currents are confined to the channel edges, becoming significant only in the tapered regions of the channel. Finally, the effect of polymer concentration on retention is more pronounced in mixed carrier liquids.

INTRODUCTION

In field-flow fractionation (FFF), components are separated due to their differential interaction with an applied field.[1] That interaction can be defined by two opposing motions: 1) the movement of material in response to the applied field, and 2) the diffusion of material away from the concentration buildup arising from the field-induced motion. The analyte properties that govern the former motion depend on the nature of the applied field and, therefore, differ among FFF subtechniques. For example, sedimentation FFF separates materials according to their buoyant mass, while electrical FFF separates material according to their charge. Regarding the latter motion, diffusion is a factor in all FFF subtechniques. Therefore, in the application to macromolecules and submicron-sized particles, where diffusion is significant, all FFF subtechniques separate material according to size or molecular weight, in addition to the parameter(s) that govern(s) the field-induced motion.

In thermal FFF (ThFFF), the applied field is a temperature gradient. The movement of material in a temperature gradient, which is referred to as thermal diffusion, depends on the chemical composition of both the analyte and the carrier liquid.[2] As a result, composition has a direct influence on the ThFFF separation.[3-5] This is in contrast to size exclusion chromatography (SEC), where the role of polymer composition is a relatively minor one, affecting retention only by its influence on polymer conformation, which can influence diffusion and, therefore, retention. Although the separating power in ThFFF depends on the polymer-solvent couple, the separation of molecular weights above 100,000 g-mol^{-1} is generally more efficient in ThFFF compared to SEC.[6,7] On the other hand, ThFFF has a lower limit to the molecular weight range that can be separated. The lower limit varies with the polymer, but is generally a few thousand g-mol^{-1}. Molecular weights below 3000 g-mol^{-1} can been separated by ThFFF,[8] but the large temperature gradients necessary for such applications require the channel to be pressurized in order to raise the boiling point of the carrier liquid. Pressurization requires specialized equipment that is more costly and cumbersome. Thus, ThFFF cannot replace SEC as a general method for the analytical separation of polymers, rather the two techniques are complementary.

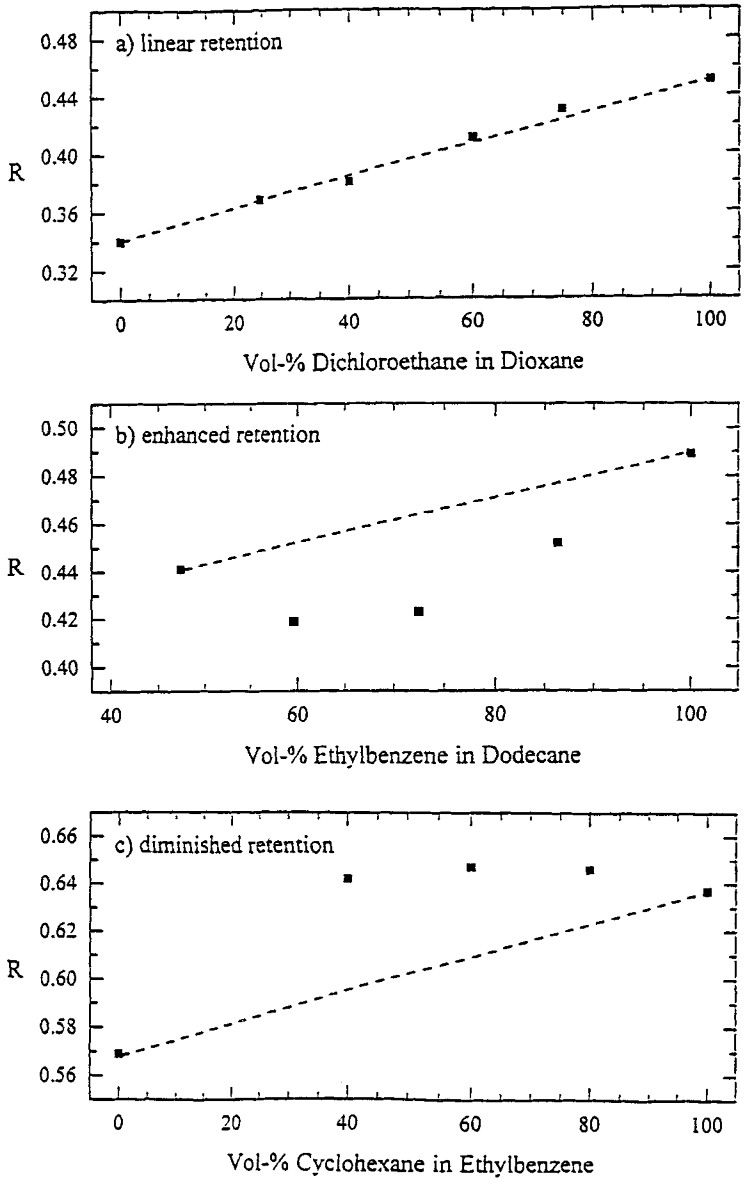

Figure 1. Plots of retention ratio R versus solvent composition in carrier-liquid mixtures, illustrating (a) linear dependence, (b) enhanced retention, and (c) diminished retention.

The lack of dependence of thermal diffusion on molecular weight in dissolved polymers[9] simplifies the characterization of molecular weight in such materials because the relationship between diffusion and molecular weight has been defined for many polymer-solvent systems. Even when such a relationship has not been defined, it can be established using size exclusion chromatography[10] or viscosity measurements.[11] Although a poor understanding of thermal diffusion has hindered full utilization of the compositional selectivity of ThFFF, recent improvements in that understanding have allowed for the development of methods to characterize the composition of certain copolymers.[12]

ThFFF typically employs a homogeneous carrier liquid. The first reported use of solvent mixtures involved mixtures of dimethylsulfoxide and water.[13] Later, Kirkland et al.[14] reported that certain mixtures can be used to raise polymer retention to levels not previously seen. In a systematic study by Sisson and Giddings,[15] the dependence of polymer retention on solvent composition in mixed carrier liquids was found to vary widely among different solvent mixtures. Figure 1 illustrates the three different types of relationships found between retention and solvent composition. In mixtures of dichloroethane (DCE) and dioxane, retention is a linear function of solvent composition. In mixtures of ethylbenzene (EB) and dodecane (DoD), the dependence of retention on solvent composition deviates from linearity toward lower R-values; this is subsequently referred to as enhanced retention, since lower R-values correspond to higher levels of retention. By contrast, the dependence of retention on solvent composition deviates from linearity toward lower levels of retention (higher R values) in mixtures of EB and cyclohexane (CYH); this behavior is subsequently referred to as diminished retention. Enhanced retention can be used to lower the molecular weight range to which ThFFF can be applied. Figure 2 illustrates the separation of five polystyrene standards, ranging in molecular weight from 2500 to 179,000 g-mol^{-1}, in a mixture containing 45 vol-% tetrahydrofuran (THF) in DoD. This fractogram represents the lowest molecular weight polymer ever resolved from the void peak without channel pressurization.

The enhanced retention of polymers in mixed carrier liquids appears to result from a synergistic effect that involves the thermal diffusion of both polymer and solvent. If the two components have different solvating powers for the polymer, retention is enhanced when the better solvent partitions in the same direction (to the cold wall) as the polymer. When the better solvent partitions to the hot wall, retention is diminished. Thermodynamic calculations confirm the significance of this solubility-based driving force, and the so-called partitioning effect was demonstrated in several carrier liquid mixtures,[16] including those represented in Figure 1. For example, in mixtures of EB and

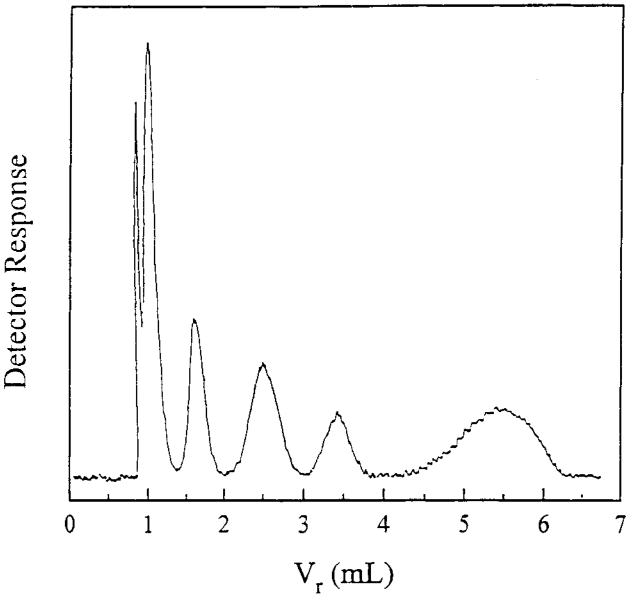

Figure 2. Separation of polystyrene components using a mixture of 45 vol-% THF in DoD as the carrier liquid. From left to right, the first peak is the void peak; successive peaks contain polystyrene standards of the following molecular weights, in thousands (k): 2.5k; 20k, 47k, 97k, and 179k. Reproduced with permission from Reference 16.

CYH, the better solvent (EB) partitions to the hot wall and retention is diminished, while in mixtures of EB and DoD, the better solvent (EB) partitions to the cold wall and retention is enhanced. In each of seven cases examined thus far, the dependence of polymer retention on solvent composition is consistent with the proposed mechanism.

The first series of liquid mixtures in which the partitioning effect was studied in detail involved DCE and CYH. The partitioning of an 81.8 vol-% mixture of DCE in CYH is illustrated in Figure 3. Plots like those in Figure 3 are obtained by exposing solvent mixtures to a temperature gradient as they flow through a specialized ThFFF channel. The channel contains a single inlet and two outlets, one at each (hot and cold) wall. The composition of the solvent layers at the hot and cold walls is sampled at the channel outlets. Thin layers at each wall are sampled by adjusting the back pressure at each outlet with needle valves, which allows the fraction of total flow eluting from each outlet (referred to as the split ratio) to be precisely controlled.

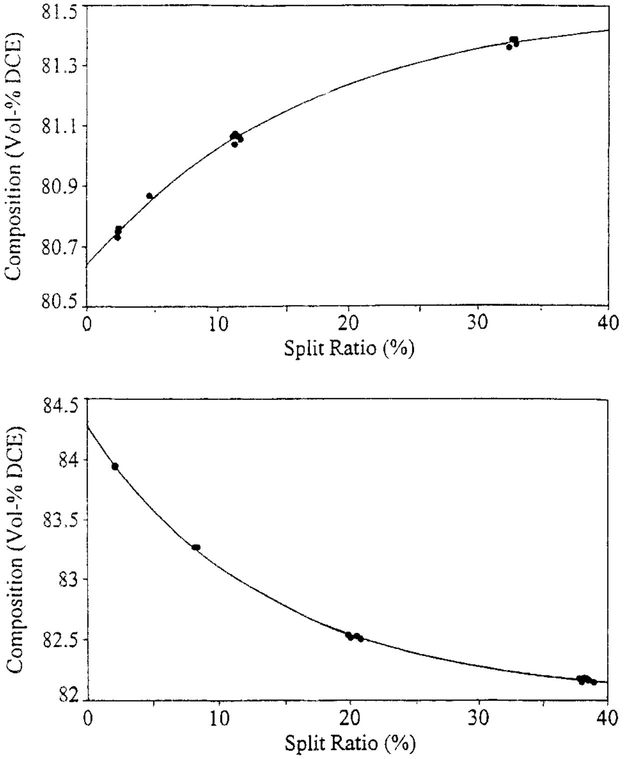

Figure 3. Measured concentration of DCE eluting from the outlets of a channel in the normal orientation (hot wall up) as a function of the split ratio in mixtures of 81.8 vol-% DCE in CYH. The solid lines represent a fit of the data to an exponential function: top, depletion (hot) wall; bottom, accumulation (cold) wall. Reproduced with permission from Reference 16.

The use of liquid mixtures to enhance polymer retention in ThFFF would benefit from a better understanding of thermal diffusion in liquids. In the work discussed above,[16] the partitioning of 12 solvents in 25 different binary combinations was measured. With the exception of CYH, the relative tendency of a solvent to partition to the cold wall follows the order of increasing density. An analysis of variance signifies the role of density at the 99% confidence level. Variance analysis also indicates that solvent partitioning is affected (99% confidence) by the solvent's activation energy for viscous flow, which is the coefficient in the exponential dependence of viscosity on temperature. Both correlations are consistent with previous studies of thermal diffusion in polymers solutions,[10] where a significant fit was found in regressing the thermal diffusion coefficient (D_T) of the polymer to a function of the polymer density and the viscous activation energy of the solvent.

Since solvent partitioning is correlated to density, we must consider the existence of convective motions in the fluid. Convection is a macroscopic displacement caused by density gradients and is a process separate from thermal diffusion.

With homogeneous liquids, convection should be negligible in thin ThFFF channels, even though a small density gradient is induced by the temperature gradient. However, in mixed solvents, larger density gradients are possible due to solvent partitioning. Convective motions in mixed solvents may lead to instabilities in the concentration profiles established by thermal diffusion. Normally, the ThFFF channel is oriented with the cold wall down. In this case, when the denser liquid thermally diffuses to the cold wall, convective forces reinforce partitioning due to thermal diffusion.

However, if the denser liquid were to thermally diffuse up to the hot wall, convection could lead to remixing of the liquid components. In fact, we cannot rule out the possibility that convective instabilities completely counteract any partitioning due to thermal diffusion in the majority of cases where the denser liquid thermally diffuses to the hot wall. Therefore, the observed correlation between partitioning and density may be an artifact of convective motion in the channel.

The objective of the work reported here is to address the issue of convective motion while evaluating the role of density in thermal diffusion and polymer retention. Our approach is to measure both solvent partitioning and polymer retention in a ThFFF channel whose orientation has been reversed, so that the cold wall lies above the hot wall.

The results will be compared to those obtained with a channel oriented in the normal configuration. If thermal diffusion is governed by density at a fundamental level, then solvent partitioning and polymer retention will be unaffected by channel orientation in the absence of convective motion.

Even if convection is present, it may not affect polymer retention if it is confined to the edges of the channel. If, on the other hand, density plays a role that is separate from thermal diffusion, both solvent partitioning and polymer retention will be affected by channel orientation.

THEORY

Thermal Diffusion in Liquids and Polymer Solutions

The reader is referred to the literature for a detailed discussion of thermal diffusion in liquids.[17] In summary, attempts to present a unified, rigorous theory of thermal diffusion in condensed-state matter have been unsuccessful. As a result, the approach to defining thermal diffusion in liquids remains phenomenological. This approach states that the movement of material in a temperature gradient is governed by the balance of two opposing transport mechanisms. The thermal gradient along coordinate x causes transport toward one wall; as a concentration gradient is formed, mass diffusion serves as a counteracting transport mechanism. The balance of these two mechanisms yields the following concentration profile

$$c(x) = c_o \exp\left[\frac{D_T(dT/dx)}{D}x\right] \tag{1}$$

where D_T and D are the thermal and ordinary diffusion coefficients, respectively, dT/dx is the temperature gradient, and c_o is the concentration at the accumulation wall. Thus, a component's highest concentration is at the accumulation wall, decreasing exponentially away from the wall. The ratio D_T/D is referred to as the Soret coefficient. In binary mixtures, a similar equation is defined for each component, and the two equations are combined to yield the following extent of separation in an open cell

$$\frac{C_H(1-C_C)}{C_C(1-C_H)} = \exp\left[\frac{D_T\Delta T}{D}\right] \tag{2}$$

Here C_H and C_C are the concentrations of one of the components at the hot and cold walls, respectively, and ΔT is the temperature difference between the hot and cold walls. Thus, the extent of separation is governed by the Soret coefficient and ΔT. Values of the Soret coefficient for liquid mixtures have been measured in the range of 0.001 to 0.1 K^{-1}. For a mixture with an initial concentration ratio of 10:90 and a Soret coefficient of 0.01, the more dilute component will be enriched to 13:87 at the hot wall and diluted to 7:93 at the cold wall when the temperature difference is 50 K. Thermodynamic calculations, supported by empirical evidence, indicate that even this small difference in solvent composition affects the free energy of polymer solutions to a significant degree.[16]

Relaxation Time

In order to obtain precise values for the Soret coefficient, sufficient time must be allowed for the liquid to partition to its steady-state concentration profile under the influence of the temperature gradient. According to Von Halle,[18] the approach to steady state in a static thermal diffusion cell is exponential with a relaxation time approximated by

$$\tau = w^2/D\pi^2 \tag{3}$$

where w is the thickness of the cell (or ThFFF channel). Assuming a diffusion coefficient of 10^{-5} cm^2/s, Eq. 3 predicts a relaxation time on the order of 10 s for the channel and conditions used in this work. At a flow rate of 0.6 mL/min, the solvent is in the channel for 225 s, yet in previous work with the normal orientation, partitioning continued to increase with residence times beyond 350 s. Unfortunately, we cannot keep the liquids in the channel for longer periods of time without losing satisfactory precision in our measure of solvent partitioning. Therefore, we did not attempt to obtain Soret coefficients in this work. However, by keeping the field strength and flow rate constant, while precisely controlling and measuring the outlet-split ratio, we are able to make qualitative comparisons required to evaluate the effect of channel orientation on thermal diffusion.

ThFFF Retention

In dilute polymer solutions, the opposing forces of thermal and ordinary diffusion result in a concentration profile that decreases exponentially away from the cold wall. The center of mass of the profile is defined by its distance ℓ from the cold wall. For mathematical convenience, ℓ is expressed in dimensionless form $\lambda = \ell/w$, which is related to the transport coefficients by

$$\lambda = \frac{D}{wD_T(dT/dx)} \approx \frac{D}{D_T\Delta T} \tag{4}$$

Using the velocity profile of the carrier liquid, which is well defined in FFF because the flow is laminar, the volume V_r of carrier liquid required to flush a polymer component through the channel is related to λ as follows:

$$R = \frac{V^o}{V_r} = 6\lambda(\coth\frac{1}{2\lambda} - 2\lambda) \tag{5}$$

Here V^{o} is the void volume and R is termed the retention ratio. In the limit of high retention, the term in parentheses on the right side of Eq. 5 approaches one and Eqs. 4 and 5 can be combined to yield

$$R = \frac{1}{6\Delta T(D_T / D)} \tag{6}$$

Thus, a polymer's retention ratio varies directly with its Soret coefficient.

MATERIALS AND METHODS

The ThFFF instrument is similar to the FFFractionation Model T-100 (Salt Lake City, USA), except that temperature control is achieved using a proportional counter described previously.[16] The channel has a tip-to-tip length of 46 cm and a breadth of 2.0 cm. Two different channel thicknesses were used. For measuring the partitioning of solvent mixtures, we used a 254 μm-thick channel (void volume 2.25 mL) with a single inlet and two outlets. The flow rate through the channel was 0.60 mL/min. As described above, the composition of solvent layers were sampled at both channel outlets as the ratio of solvent out each wall was varied. The sampling port at each wall consisted of a t-union with a rubber septum, placed just upstream from the needle valves used to control the split ratio. The effluent was sampled by penetrating the septum with a microliter syringe. The collected effluent was injected directly into a gas chromatograph for analysis. This arrangement precluded selective evaporation of one component prior to analysis.

For measuring polymer retention, we used a 102 μm-thick channel with a resulting void volume of 0.90 mL. The flow rate of the carrier liquid was 0.20 mL/min and the concentration of the injected polymer solutions was 1.0 mg/mL. Sample detection was achieved with Polymer Laboratories (Amherst, MA) Model 950/14 evaporative mass detector. The polystyrene standards came from either Supelco Co. (Bellefonte, USA) or Pressure Chemical Co. (Pittsburgh, USA).

Samples were relaxed into their steady-state distributions at the accumulation wall using the stop-flow technique with a relaxation time of 1 min. In computing R from Eq. 5, V_r was calculated by subtracting the volume of the inlet and outlet tubing from the total volume of carrier liquid required to flush the sample from injector to detector. The void volume V^{o} was equated to the retention volume of a polymer standard in the absence of an applied field.

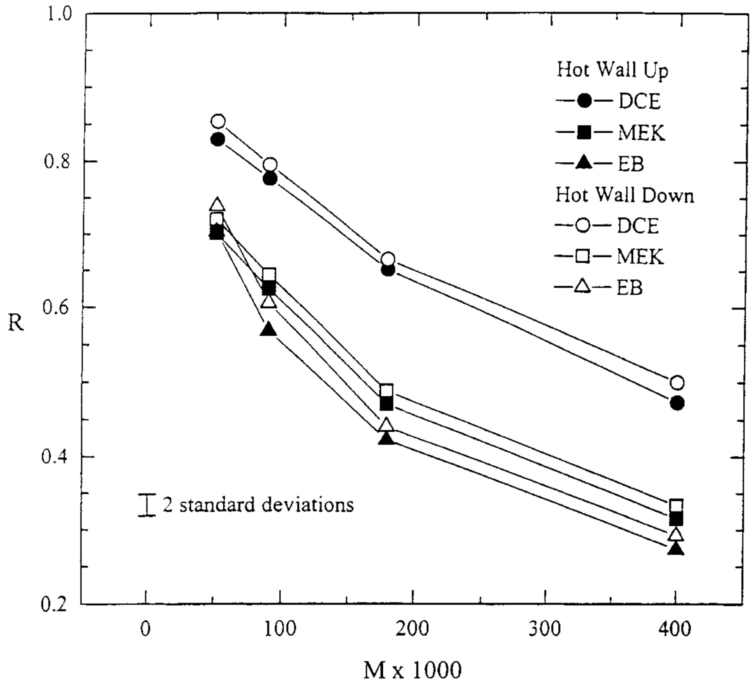

Figure 4. Plots of retention ratio R versus molecular weight M in homogeneous carrier liquids, illustrating the independence of retention on channel orientation.

RESULTS AND DISCUSSION

As we mentioned above, the retention of polymers in homogeneous solvents is highly correlated to polymer density. If thermal diffusion is governed by density in a fundamental way, i.e., there is not a separate density effect, then retention will not change with channel orientation. Figure 4 compares the retention of polystyrene standards ranging in molecular weight from 50,000 to 400,000 g-mol^{-1} in three different solvents. For each of the 12 polymer-solvent systems, the difference in retention with channel orientation is not greater than the empirically-defined uncertainty of the measurement, which lies in the range of 1-3%. However, if the entire data set is considered, there does appear to be a small effect, since R values are consistently higher in the inverted orientation. Still, the differences are very small (< 2%), and for all practical purposes they are negligible. We can conclude, therefore, that density is a significant predictor variable for the thermal diffusion of polymers in solution.

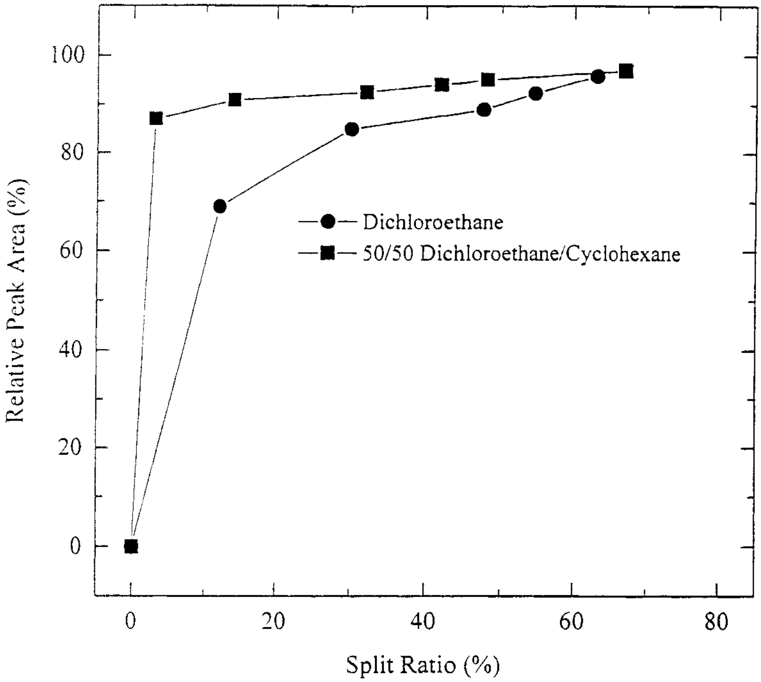

Figure 5. Plots of the relative amount of polymer eluting from the cold wall of an inverted channel as a function of the split ratio at that wall.

To confirm that the polymer does in fact move up to the cold wall in the inverted orientation, we split the outlet flow and quantified the amount of polymer eluting from the cold wall at several different split ratios. The results obtained in both a homogeneous carrier liquid (DCE) and a mixed carrier liquid (50/50 DCE/CYH) are illustrated in Figure 5. In a 50/50 (vol-%) mixture of DCE and CYH, 90% of the polymer is recovered by splitting only 15% of the carrier out the cold wall, indicating that the polymer is concentrated at that wall. In pure DCE, a larger split ratio is required to recover an equivalent amount of polymer because the mean layer thickness of the relaxed zone is greater, as indicated by a lower level of retention.

In the next series of experiments, we measured the partitioning of liquid mixtures after exposing them to a temperature gradient while they flowed through an inverted ThFFF channel. As we discuss above, measurements of the Soret coefficients are hindered by the dependence of solvent partitioning on flow rate. Accurate values of the Soret coefficients would require varying both

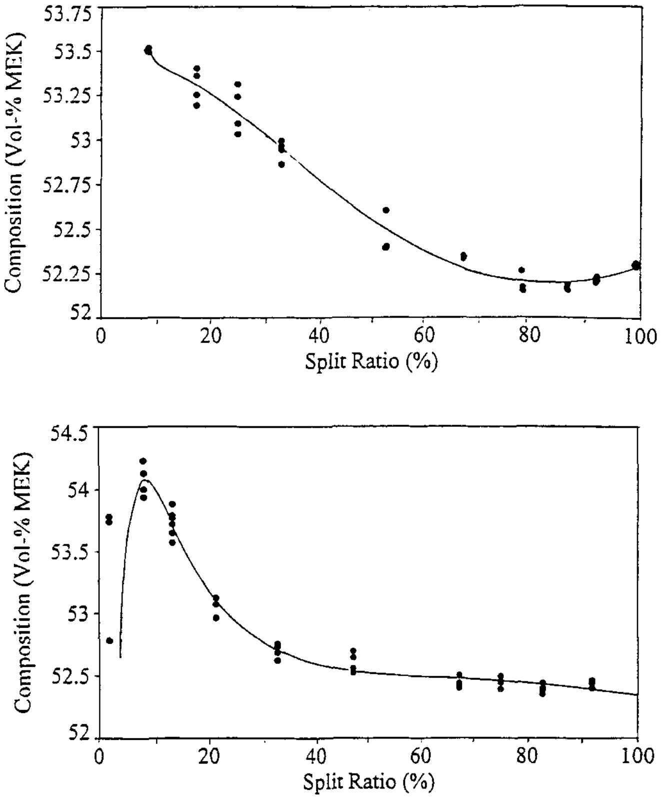

Figure 6. Measured concentration of MEK eluting from the outlets of an inverted channel as a function of the split ratio in mixtures of 52.4 vol-% MEK in CYH. The solid lines represent the best fit of the data using Tablecurve® software.

the split ratio and flow rate, so that multivariate regression methods could be used to obtain the solvent composition as both variables approach zero. Since the time required to produce such data would preclude the examination of several different liquids, while our primary objective is to compare partitioning in normal and inverted channel orientations, we opted to settle for qualitative information rather than take the time to measure precise values of the Soret coefficients.

Although the partitioning of several liquid mixtures was measured, we chose to focus on mixtures containing CYH because in the normal orientation this solvent proved to be an exception to the general trend of the denser solvent partitioning to the cold wall. Thus, CYH was enriched at the cold wall when

Table 1

Summary of the Partitioning of Binary Solvent Mixtures in an Inverted ThFFF Channel

		----- Hot Wall -----			----- Cold Wall -----		
Solvent Pair[a]	Component Enriched at Walls	Inlet Comp.[b,c]	Split Ratio[b] (%)	Wall Comp.[b,c]	Inlet Comp.[b,c]	Split Ratio[b] (%)	Wall Comp.[b,c]
DoD-CYH	DoD	50.9% DoD	2.4	53.5% DoD	50.4% DoD	2.5	51.1% DoD
EB-CYH	EB	50.0% EB	4.3	50.7% EB	49.8% EB	2.7	50.5% EB
BEN-CYH	BEN	51.0% BZ	3.1	51.3% BZ	51.1% BZ	2.9	51.6% BZ
MEK-CYH	MEK	49.4% MEK	1.4	51.1% MEK	48.9% MEK	2.7	50.8% MEK
CYH-THF	CYH	49.8% CYH	2.5	50.1% CYH	50.3% CYH	2.3	50.5% CYH
CYH-CCl_4	CYH	50.3% CYH	1.8	51.4% CYH	50.2% CYH	2.0	50.7% CYH
CYH-DCE	CYH	51.4% CYH	1.4	52.2% CYH	51.3% CYH	2.0	51.8% CYH
DoD-MEK	DoD	48.3% DoD	6.0	49.1% DoD	48.5% DoD	6.4	49.3% DoD
DoD-CCl_4	DoD	51.0% DoD	1.2	52.0% DoD	51.5% DoD	1.2	52.9% DoD
MEK-EtOH	MEK	48.8% MEK	2.0	50.3% MEK	48.8% MEK	2.0	49.8% MEK

[a] key: DCE, 1,2-dichloroethane; CYH, cyclohexane; EB, ethylbenzene; BZ, benzene; MEK, 2-butanone; THF, tetrahydrofuran; DoD, n-dodecane; EtOH, ethanol. [b] Standard error is 0.2%. [c] Compositions are in volume percent.

mixed with the denser liquids ethyl acetate, benzene (BZ), EB, and MEK.[16] Figure 6 contains plots of the outlet composition versus the split ratio at both walls for a mixture of 52.4 vol-% MEK in CYH using an inverted channel orientation. Unlike the results obtained with a normal channel orientation (see Figure 2), the partitioning profiles measured with an inverted orientation do not follow a simple exponential form. The solid lines in Figure 6 are the best-fit functions obtained from Tablecurve® (Jandell Scientific, San Rafael, CA, USA). The unusual profiles arise from the presence of convection currents in the channel. Convection currents plagued early studies of thermal diffusion in static cells and, in fact, play an integral role in the separation of polymers by the vertically-oriented Clusius-Duckel column.[19] However, for measuring Soret coefficients, convection is undesirable, and later studies of thermal diffusion indicated that convection currents could be avoided by the use of ultra-thin (<500 μm) cylindrical cells with high aspect ratios.

By sampling in the top-center of such cells, the potential existence of convective remixing near the edges was not a concern. However, in the ThFFF channel, convective remixing near the channel edges will be augmented in the tapered region of the channel near the exit ports. Although we did not measure the partitioning of MEK/CYH mixtures in detail with the normally oriented ThFFF channel, we did confirm that MEK is enriched at the hot wall and

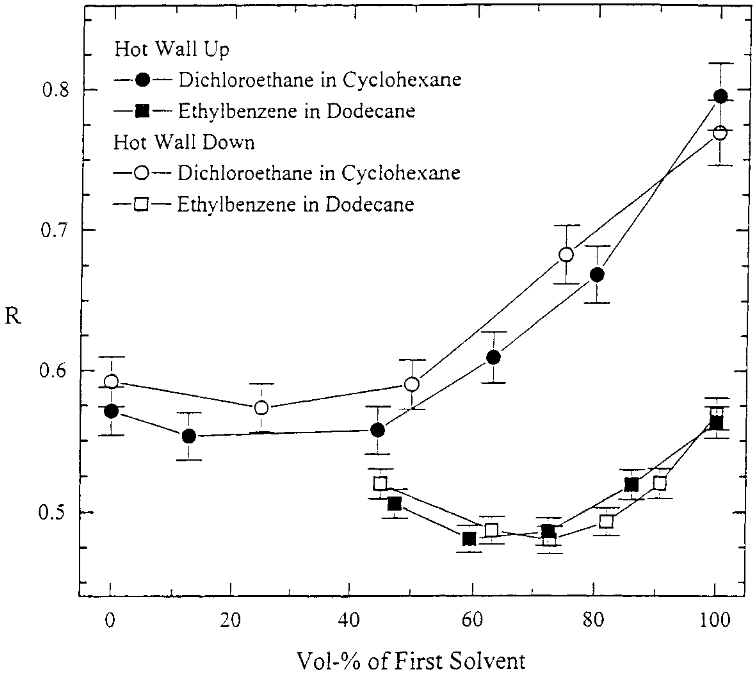

Figure 7. Retention ratio versus solvent composition in normal and inverted channel orientations, obtained with solvent mixtures that enhance retention. The polymer is 90,000 g-mol^{-1} polystyrene.

depleted at the cold wall. To determine whether the unusual behavior of MEK/CYH in an inverted channel is unique, we measured the partitioning of several other mixtures with the inverted orientation. The results are summarized in Table 1. The partitioning of each mixture represented in Table 1 was previously measured with the normal channel orientation. In each case, the solvent that is depleted from the cold wall in the normal orientation appears to be enriched at both walls in the inverted orientation.

If solvent partitioning in a ThFFF channel is truly different in the normal and inverted orientations, then the retention of polymers in mixed carrier liquids should be affected by channel orientation. This is not the case, however, as illustrated in Figure 7, which compares polystyrene retention as function of solvent composition in mixtures of DCE/CYH and EB/DoD using both channel orientations. In each mixture, the enhanced retention behavior is not affected by channel orientation. Thus, even though measurements indicate that the solvents partition differently depending on channel orientation, the differences have little effect on polymer retention. Either polymer retention is unaffected by solvent partitioning, i.e., the partitioning effect is nonexistent, or convection currents are localized to the edges of the channel so that solvent partitioning in the bulk of the channel is unaffected by channel orientation. The latter explanation is supported by thermodynamic calculations, which indicate that even small amounts of solvent partitioning affect the free energy of the solution and, therefore, polymer retention should be affected as well. The dilemma may be solved by comparing solvent partitioning in different orientations with a static thermal diffusion cell. We are currently looking at sampling methods that will allow us to utilize a modified ThFFF channel for such measurements.

The effect of composition and channel orientation on retention in mixtures of MEK and CYH is illustrated in Figure 8. Also illustrated in Figure 8, is retention in mixtures of CYH and EB. In both cases, the better solvent partitions to the hot wall when the channel is oriented with the hot wall above the cold wall. Consistent with all solvent mixtures previously examined, retention is diminished in the CYH-EB system. In the CYH-MEK system, however, the dependence of retention on solvent composition takes a sigmoidal form. Of the 13 solvent mixtures that have been examined in this or previously published works,[15,16] CYH-MEK is the first mixture to exhibit such behavior.

Finally, we examine the effect of polymer concentration on retention. It is well known that polymer retention increases above that predicted by retention theory when the concentration of the injected polymer solution is above the critical concentration where chain entanglement occurs. In order to obtain consistent results, it is necessary to work with polymer solutions below the critical concentration. When analyzing a new sample, the concentration of the injected sample should be varied. If retention decreases with sample dilution, the sample should be further diluted until retention is no longer affected. The critical concentration increases with decreasing molecular weight, but for polystyrene, concentration effects are generally absent for molecular weights below 10^6 g-mol^{-1} when the injected concentration is below 3 mg/mL.

The proposed partitioning effect for enhanced retention of polymers in mixed solvents is based on the idea that solvent gradients act as a second force on the polymer due to differences in solvation energy. The solvation energy depends on the polymer concentration. Therefore, if the partitioning effect is valid, we can expect more pronounced concentration effects in mixed carrier liquids compared to homogeneous carriers. Figure 9 compares plots of retention versus polymer concentration in THF to similar plots in mixtures of THF and DoD. In both cases, the polymer is 90,000 g-mol^{-1} polystyrene and ΔT is 47 K. The concentration effect is clearly more pronounced in the mixed

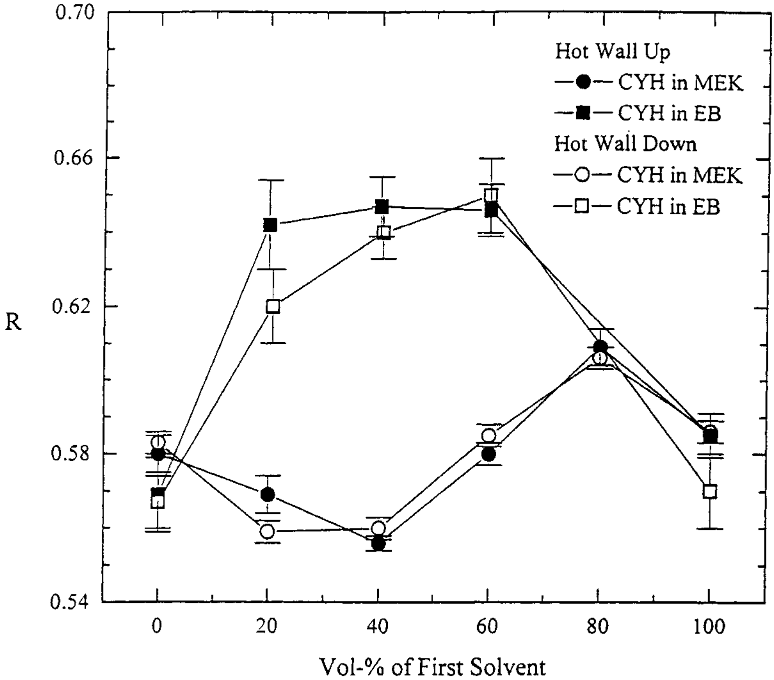

Figure 8. Retention ratio versus solvent composition in normal and inverted channel orientations, obtained with solvent mixtures in which the better solvent for the polymer partitions to the hot wall. The polymer is 90,000 g-mol^{-1} polystyrene.

solvent, with R decreasing by 10% between polymer concentrations of 1 and 10 mg/mL. In pure THF, retention decreases only 2.5% over the same concentration range. Furthermore, the concentration at which R-values level off is lower in the mixed solvent. These results further support the partitioning theory for enhanced polymer retention in mixed solvents. The results also indicate that concentration effects must be closely monitored in mixed solvents.

CONCLUSIONS

The purpose of this study was to determine whether channel orientation affects polymer retention while furthering our understanding of thermal diffusion. Regarding the latter purpose, our specific objective was to scrutinize the apparent role of density. As for the thermal diffusion of polymers, the fact that polymer retention is not affected by channel orientation means that a separate density effect does not exist. The correlation of thermal diffusion to density must therefore be considered in the development of a working model for estimating D_T-values. Such a model is highly desirable because it will allow polymer retention to be predicted from fundamental physicochemical parameters of the polymer-solvent system.

Results from the measurement of solvent partitioning are less satisfying. In contrast to the study of thermal diffusion in polymers, it has become apparent that a ThFFF channel is not the ideal tool for measuring the Soret coefficients of liquids. Even qualitative information is difficult to obtain without ambiguity in an inverted channel, due to the presence of convection currents. However, the behavior of liquid mixtures is clearly different in channels with normal and inverted orientations. In the normal orientation, the denser solvent usually partitions to the cold wall, although cyclohexane mixtures are an exception. Furthermore, the solvent that is depleted from the cold wall in the normal orientation appears to partition to both walls when the channel is inverted. While this indicates the presence of convection currents, polymer retention is not affected by channel orientation. Taken together, these two results contradict the partitioning theory, which states that retention is enhanced or diminished in mixed solvents due to solubility-based forces that arise when solvents partition in a thermal gradient. However, we must consider that convection currents established in the inverted orientation are confined to the edges of the channel. Solvent partitioning in the bulk of the channel may not be affected by channel orientation, in which case the mechanism of thermal diffusion is similar in solvent mixtures and polymer solutions, and the partitioning theory remains a valid explanation for enhanced (or diminished) polymer retention in liquid mixtures.

It is worth noting that convection appears in the inverted channel with liquid mixtures regardless of which component partitions to the cold wall in the normal orientation. Thus, convection appears to be related to channel orientation rather than the relative densities of the two solvents in the mixture.

Although the retention of polymers can be enhanced by using solvent mixtures, retention is more sensitive to polymer concentration. The concentration effect can be expected to increase with molecular weight, and more study is required to establish the magnitude of this potential problem. In the meantime, users wishing to take advantage of the flexibility offered by mixed solvents must pay close attention to the concentration of injected samples. For molecular weight analysis, this means keeping concentrations small, and ensuring that retention levels remain constant when the concentration is varied.

ACKNOWLEDGMENT

This work is dedicated to the memory of the late J. Calvin Giddings, a good friend and excellent mentor. The work was funded by Grant CHE-9634195 from the National Science Foundation.

REFERENCES

1. J. C. Giddings, Science, **260**, 1456-1465 (1993).

2. M. E. Schimpf, Trends Polym. Sci., **4**, 114-121 (1996).

3. J. J. Gunderson, J. C. Giddings, Macromol., **19**, 2618-2621 (1986).

4. G. Liu, J. C. Giddings, Chromatographia, **34**, 483 (1992).

5. S. K. Ratanathanawongs, P. M. Shiundu, J. C. Giddings, Coll. Surf. A, **105**, 243-250 (1995).

6. J. J. Gunderson, J. C. Giddings, Anal. Chim. Acta, **189**, 1-15 (1986).

7. G. Stegeman, A. C. van Asten, J. C. Kraak, H. Poppe, R. Tijssen, Anal. Chem., **66**, 1147-1160 (1994).

8. J. C. Giddings, L. K. Smith, M. N. Myers, Anal. Chem., **47**, 2389-2394 (1975).

9. M. E. Schimpf, J. C. Giddings, Macromol., **20**, 1561 (1987).

10. M. E. Schimpf, J. C. Giddings, J. Polym. Sci., Polym. Phys. Ed., **27**, 1317 (1989).

11. J. J. Kirkland, W. Rementer, Anal. Chem., **64**, 904-913 (1992).

12. M. E. Schimpf, "Determination of Molecular Weight and Composition in Copolymers Using Thermal Field-Flow Fractionation Combined with Viscometry," in **Chromatographic Characterization of Polymers: Hyphenated and Multidimensional Techniques**, T. Provder, H. G. Barth, M. W. Urban, eds., American Chemical Society, Washington, D. C., 1995, Vol. 247, pp. 183-196.

13. M. N. Myers, K. D. Caldwell, Sepn. Sci., **9**, 47-70 (1974).

14. J. J. Kirkland, L. S. Boone, W. W. yau, J. Chromatogr., **517**, 377-393 (1990).

15. R. M. Sisson, J. C. Giddings, Anal. Chem., **66**, 4043-4053 (1994).

16. C. A. Rue, M. E. Schimpf, Anal. Chem., **66**, 4054-4062 (1994).

17. J. E. Powers, in **Separation and Purification Methods**, E. S. Schoen, ed., Wiley-Interscience, New York, 1962, Vol. 1-98.

18. E. Von Halle, AEC Research and Development Report, K-1420 (1959).

19. P. Debye, A. M. Bueche, **High Polymer Physics**, Chemical Publishing Co., New York, 1948.

Received January 28, 1997
Accepted April 24, 1997
Manuscript 4452