MEASUREMENT OF THERMAL DIFFUSION PARAMETERS OF POLYSTYRENE USING A THERMAL FIELD FLOW FRACTIONATION METHOD

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Abstract— Thermal diffusion parameters such as the thermal diffusion factor and the thermal diffusion coefficient for polystyrene in toluene are measured by using a thermal field flow fractionation (TFFF) method. The dependence of these parameters upon temperature, concentration, and polymer molecular weight is examined.

The thermal diffusion coefficient is found to be independent of the molecular weight for sufficiently large polymer molecules, but on the other hand the ordinary diffusion coefficient is known to be pronouncedly dependent on the molecular weight.

This result indicates that the fractionation effect is primarily governed by the differences in ordinary diffusion coefficients.

INTRODUCTION

The study of thermal diffusion in the thermofractionation of polymer solution stems from the work of Debye and Bueche [1], who exhibited a large thermal diffusion effect in a Clusius-Dickel column. In 1960, Ham proposed a kinetic theory for the thermofractionation of polymer solution [2]. Concerning the thermal diffusion factor a and the thermal diffusion coefficient D′, Ham's theory predicts

$$a = \frac{E_s D_s}{R'TD} \; ; \quad D' = \frac{E_s D_s}{R'T^2} \qquad (1)$$

where D_s and E_s are the self diffusion coefficient and the activation energy of pure solvent, respectively. It means that, for sufficiently high molecular weights, the thermal diffusion coefficient D′ depends only upon the properties of the pure solvent and, in particular, is independent of the molecular weight and the concentration of polymers.

In addition to the kinetic theory, several workers studied the thermal diffusion in polymer solutions by using various experimental methods [3-9]. Langhammer [3] used the Clusius-Dickel column with convection and placed a solution between two vertical plates kept at different temperatures. Emery and Drickamer [4] and

Whitmore [5] placed the solution between the horizontal plates of different temperatures. Meyerhoff and Nachtigall [6] also used the static cell. but they determined the concentration distribution with an optical method. Rauch and Meyerhoff [7], Hoffman and Zimm [8], and Herren and Ham [9] used the moving boundary method with a convection-free thermodiffusion cell. In addition to these methods, the thermal diffusion parameters can be determined by a thermal field flow fractionation (TFFF) method which was first devised by Giddings in 1966 [10].

The TFFF is a separation method of macromolecules that a temperature gradient is applied across a channel through which a solvent flows [11]. A differential retention of the solute in a TFFF column leads to separation and makes it possible to measure thermal diffusion parameters [12]. In these measurements, the TFFF method has several advantages [13] over other techniques described above: minute sample requirements, relatively less time for measuring thermal diffusion parameters, and simultaneous fractionation.

In the present work, the thermal diffusion parameters are measured by using the TFFF method. Empirical equation for the ordinary diffusion coefficient is very much related to the polymer molecular weight [12]. However, it is still unclear that the thermal diffusion coefficient depends upon the molecular weight and the concentration of solutes. The purpose of this work is

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to explain not only the dependence of the thermal diffusion parameters upon temperature, concentration and polymer molecular weight but also the contribution of the differences in the thermal diffusion coefficient of polymer solutes to the separation in the TFFF column.

CALCULATION OF THERMAL DIFFUSION PARAMETERS

Retention in Field flow fractionation is characterized by the retention ratio, R, which may be obtained directly from experimental chromatograms,

$$R = \frac{V_{zone}}{\langle V \rangle} \tag{2}$$

where V_{zone} stands for the mean velocity of solute zone and $\langle V \rangle$ is the average velocity of solvent. The retention ratio is related to the dimensionless parameter λ by the following equation:

$$R = 6 \lambda \left[\coth \left(\frac{1}{2\lambda} - 2\lambda \right) \right] \tag{3}$$

Here λ is the ratio of the characteristic thickness of solute layer (l) to channel width (w). In dilute solutions, the ratio λ is related to thermal diffusion by [14]

$$\lambda = 1 / \left(\frac{\alpha}{T} + \gamma \right) \frac{dT}{dx} w \tag{4}$$

where α is the thermal diffusion factor, γ is the coefficient of thermal expansion of the solution, and $\frac{dT}{dx}$ is the temperature gradient. Assuming that a linear temperature profile exists in the channel, and substituting the temperature gradient $\frac{dT}{dx}$ by $\frac{\Delta T}{w}$ eq.(4) changed to the following form:

$$\lambda = 1 / \left(\frac{\alpha}{T} + \gamma \right) \Delta T \tag{5}$$

Since $\frac{\alpha}{T} \gg \gamma$, γ can be neglected [15]. When the temperature T is substituted by the temperature of center of gravity of the solute layer $T_{c.g}$, eq.(5) becomes

$$\lambda = \frac{T_{c.g}}{\alpha \Delta T} \tag{6}$$

Under the condition of the linear temperature profile in the channel, the following equation is obtained:

$$\frac{T_{c.g} - T_c}{\Delta T} = \frac{l}{w} = \lambda \tag{7}$$

Substitution of eq.(7) into eq.(6) yields

$$\alpha = 1 + \frac{T_c}{\lambda \Delta T} \tag{8}$$

We can obtain directly the thermal diffusion factor α through the above equation. In order to calculate the value of the thermal diffusion coefficient D', the following equation defining α is used [16].

$$\alpha = \frac{D'T}{D} \tag{9}$$

Replacing T with $T_{c.g}$ yields

$$D' = \frac{\alpha D}{T_{c.g}} \tag{10}$$

Using the Einstein relationship, $D = KT/f$, applicable to a dilute solution [17], the ordinary diffusion coefficient D is obtained. Here f is the friction coefficient for molecular transport. For the polystyrene-toluene system, the ordinary diffusion coefficient calculated through this method is approximated by eq.(11).

$$D = (M. W.)^{-0.553} \exp \left(-3.8029 - \frac{1285}{T_{c.K}} \right) \tag{11}$$

According to Giddings, eq.(11) agrees comparably with experimental data for polystyrene in toluene [12]. Substituting equations (8) and (11) including the λ value, which are obtainable by experiment, into eq.(10), we can obtain the value of the thermal diffusion coefficient D'.

EXPERIMENTAL

The TFFF apparatus used in this work is in principle identical to that used by Giddings et al. [14]. A TFFF column, the main part of the TFFF system, is composed of a channel, two heat transfer metal bars forming channel walls, and support units for applying the thermal field. As a whole body, it is made by clamping two polished copper bars together over a thin poly(ethylene terephthalate) film spacer.

The channel through which the solvent is flowing is formed by cutting out a 2 cm in breadth and 41.2 cm in length with tapered ends from the poly(ethylene terephthalate) film spacer of 0.25 mm thickness.

The hot copper bar which forms the face of the channel is heated by two 500-W cartridge heaters controlled by temperature controllers. The cold bar which forms the bottom face of the channel has three holes drilled through the entire length, allowing a coolant to enter the center hole and flow out through two outer holes. Both the top and the bottom bar have several 4 mm diameter holes drilled extremely close to the surface of the channel to insert iron-constantan thermocouples for the temperature measurement.

The overall schematic diagram of this system is shown in Fig. 1. The solution of polystyrene (PS) standard is injected at the inlet of the column with a 10-μl syrindge through the injection port. Injection is made under the static condition by the stop flow method. A differential refractive index detector (Waters Associates Model R401) is used to measure the concentration of PS solutes. A constant solvent flow of 9.4 ml/hr is main-
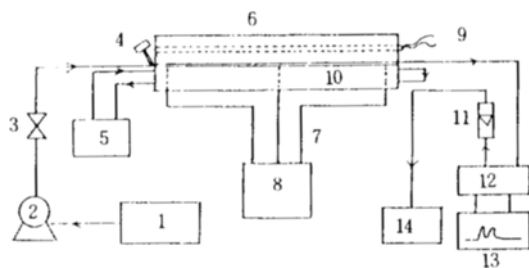
Fig. 1. Schematic flow diagram.

1. Solvent reservoir 2. High pressure pump
3. Flow restrictor 4. Injection port
5. Circulator 6. Column
7. Thermocouple 8. Temperature
9. Cartridge heater recorder
10. Channel 11. Rotameter
12. Detector 13. Recorder
14. Waste vessel

tained by a liquid chromatographic pump (Waters Associates Model 6000A). The corresponding mean solvent velocity through the channel is 0.05cm/sec.

The carrier liquid is the high purity toluene (99.99%) which is a good solvent for PS standards (Waters Associates, Inc., Milford, Mass., U.S.A.) with a narrow molecular weight distribution (polydispersity less than 1.05).

RESULTS AND DISCUSSION

In order to observe the effect of temperature on the thermal diffusion factor α, the temperature differences between the hot and the cold wall were changed from 20°C to 55°C keeping the cold wall at a constant temperature (20°C). Fig. 2 shows the dependence of α on the mean channel temperature $\bar{T}$ for three different molecular weight (M.W.) solutes. The thermal diffusion
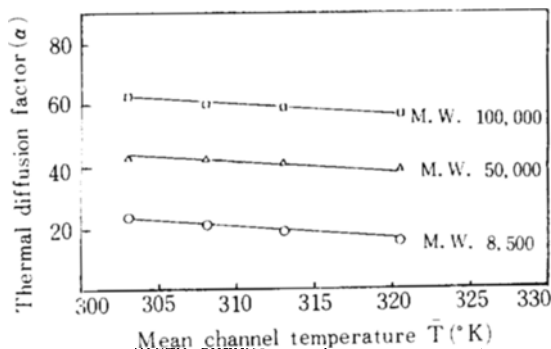

Fig. 3. The plot of thermal diffusion factor(α) versus molecular weight(M. W.) at $T_c =$ 20℃.

factor decreases almost linearly with increasing the mean channel temperature $\bar{T}$.

The dependence of the thermal diffusion factor α upon the polymer M.W. is shown in Fig. 3 for two temperature differences, 15°C and 30°C. α values show a consistent upward trend upon the polymer M.W.

In Fig. 4, the present result for α is compared with others. The figure shows a considerable lack of agreement in the dependence of α on the M.W. Our results disagrees with Drickamer's assertion [4] that α is proportional to the polymer M.W. but shows the similar value with the data of Meyerhoff and Nachtigall [6] whose results agree with Ham's theory expressed by eq.(1).

In order to ascertain the effect of temperature on the thermal diffusion coefficient D ', several experiments were performed for various differences of channel temperatures keeping the cold wall at a constant temperature (20°C). The thermal diffusion coefficient D ' is plotted against the mean channel temperature $\bar{T}$ in Fig. 5. The temperature dependence of D ' is striking and D ' shows a maximum at a mean channel temperature.

Fig. 2. The temperature dependence of thermal diffusion factor(α) for polystyrene in toluene at a fixed cold wall temperature ($T_c = 20$℃).
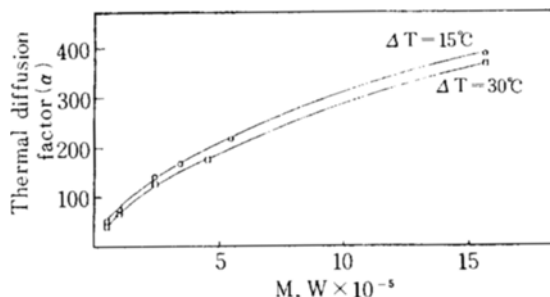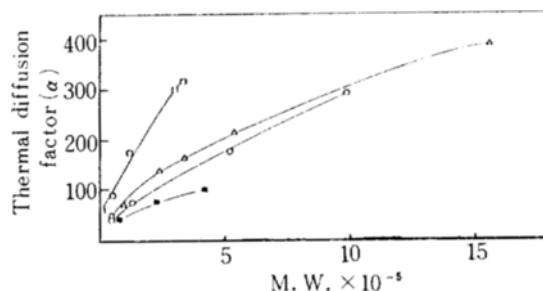

Fig. 4. Thermal diffusion factor(α) vs. molecular weight(M. W.)(□) Emery and Drickamer, $T_c = 19$℃ (△) This work, $T_c = 20$℃, $\Delta T =$ 30℃ (○) Meyerhoff and Nachtigall, $T_c = 20$℃ (■) Taylor, $T_c = 20$℃.
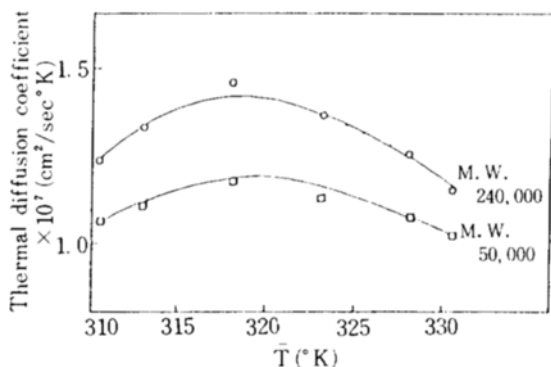
Fig. 5. The plot of thermal diffusion coefficient (D') vs. mean channel temperature ($\bar{T}$) at $T_c = 20\,°C$, $\Delta T = 30\,°C$.

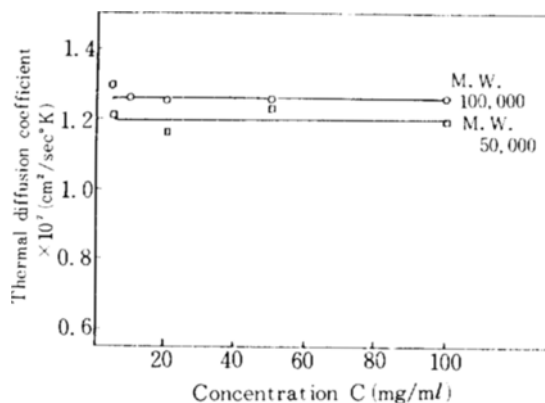Fig. 7. The plot of thermal diffusion coefficient (D') vs. the concentration of samples(C).

Thus this shows a difference from Ham's equation expressed by eq.(1) in which D' is inversely proportional to the square of temperature.

The problem of dependence of D' upon the polymer M.W. and the concentration has been rather unclear until now, but the problem is important in understanding the thermofractionation of polymers because it can explain whether this fractionation effect is primarily dependent upon D' or the ordinary diffusion coefficient D. To elucidate this problem, D' was plotted against M.W. at two temperature differences in Fig. 6. It is increased with M.W. below 240,000 but constant above it. It is nearly independent of M.W. ranging from 240,000 to 1,560,000. This result is in accord with the Ham's theory expressed by eq.(1) and agrees with the experimental result of Ham and Herren [9] which shows that D' has an almost constant value of 1.5×10^{-7} cm²/sec/°K above a M.W. 300,000
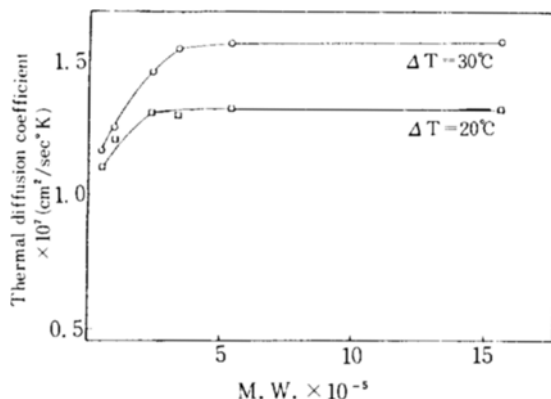
To observe the concentration dependence of D' fix-

ed quantities (10 µl) of PS samples which were previously prepared for constant concentrations ranging from 5 to 10 mg/ml are injected. The height of the solute peak increases almost linearly as the concentration of the injected sample increases. This indicates that of the injected sample is maintained constant through the whole channel as the solution flows. Thus it is possible to choose that as a variable in this experiment. We test the concentration dependence for two different M.W., 50,000 and 100,000, at a channel temperature difference $\Delta T = 30\,°C$. Fig. 7 shows that D' is nearly independent of the concentration of polymer samples. This is nearly consistent with the results of Nachtigall and Meyerhoff [6], Rauch and Meyerhoff [7], and Herren and Ham [9].

The separation of solutes in the TFFF column is resulted from the interplay of the thermal diffusion and ordinary diffusion. The thermal diffusion leads to the transport of solutes from the hot to the cold wall. As a concentration gradient is thus formed, the ordinary diffusion acts as a counteracting transport mechanism and makes solutes diffuse to the opposite direction. But as shown in above sections, the thermal diffusion coefficient governing the thermal diffusion is constant above M.W. 240,000 and independent of the concentration of polymer samples. Therefore, it can not be responsible for the thermofractionation effect of polymer solutes and only produces the required concentration gradient. On the other hand, this fractionation effect in this TFFF column is apparently governed by the differences in the ordinary diffusion coefficient of solutes whose pronounced dependence on M.W. is well known.

Fig. 6. The plot of thermal diffusion coefficient (D') vs. molecular weight(M. W.) at $T_c = 20\,°C$.

CONCLUSIONS

Through the present investigation, the following conclusions could be drawn;

1. The thermal diffusion factor shows a temperature

dependence that it decreases almost linearly with increasing the mean channel temperature.

2. The temperature dependence of the thermal diffusion coefficient is striking and has the trend that it shows a maximum at a mean channel temperature.

3. The thermal diffusion coefficient is found to be independent of the molecular weight for sufficiently large polymer molecules and the concentration of polymer solutes. But on the other hand the ordinary diffusion coefficient is known to be pronouncedly dependent on the molecular weight. This result indicates that the fractionation effect in TFFF column is primarily governed by the differences in the ordinary diffusion coefficient of solutes.

NOMENCLATURE

D   : ordinary diffusion coefficient for the solute-solvent system.
D′   : thermal diffusion coefficient
D_s : self diffusion coefficient of solvent
E_s : the activation energy of solvent
f   : friction coefficient of molecular transport
K   : gas constant divided by Avogadro number
l   : mean thickness of solute layer
M.W.   : molecular weight of solute
R   : retention ratio
R′   : gas constant
T   : temperature
T_c : cold wall temperature
$\bar{T}$: mean temperature in channel
$T_{c.g}$: solvent temperature at center of gravity
ΔT : temperature difference between the hot and cold walls
(V)   : mean carrier velocity
V_{zone} : solute zone velocity
w   : channel thickness, the distance between opposing walls

Greek Letters

α : thermal diffusion factor of solute
γ : the coefficient of thermal expansion of solution

λ : $\dfrac{l}{w}$ dimensionless layer thickness

Subscripts

c   : cold wall
c.g   : the center of gravity of solute layer
s   : solvent
zone   : solute zone

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