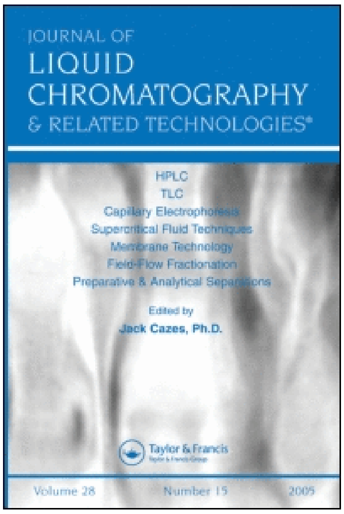

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HYDRODYNAMIC VOLUME FLUCTUATION OF POLYSTYRENE BY COLUMN TEMPERATURE AND ITS EFFECT TO RETENTION VOLUME IN SIZE EXCLUSION CHROMATOGRAPHY

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ABSTRACT

The fluctuation in hydrodynamic volume of polystyrene in several solvents was evaluated by changing solvent temperature and the relation between the magnitude of the fluctuations and the retention volume change was experimentally examined. Limiting viscosity numbers of polystyrene in tetrahydrofuran(THF), chloroform, toluene, cyclohexane, and a benzene-methanol mixed solvent (77.8/22.2 vol/vol) were measured by using a Ubbelohde-type viscometer. Temperature dependence of limiting viscosity number of the polystyrene solution was observed in some range of temperature, where a change of the retention volume of polystyrene would be assumed to be observed with the change of column temperature because of the change of its hydrodynamic volume in solution. The examination of the temperature dependence of retention volume in SEC for polystyrene standards confirmed this effect. The recommended column temperature is in the range where the temperature dependence of the limiting viscosity number of polystyrene solutions is negligible; e.g., at 25° - 50°C for THF, 35° - 65°C for toluene, and 20° - 30°C and 45° - 55°C for chloroform. Column temperature in the range of 30° - 45°C in chloroform is also recommended because of counterbalance of several effects to retention volume fluctuation.

INTRODUCTION

The measurement of molecular weight averages and their distributions for polymers by size exclusion chromatography (SEC, or GPC)

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requires the construction of a calibration curve obtained by plotting retention volumes vs. molecular weight of the corresponding polymers. A reliable molecular weight - peak retention volume relationship is the most important factor for obtaining the accurate and precise molecular weight averages. The retention volume changes with changing column temperature [1,2]. In the previous paper [3], we reported the effect of column temperature on the retention volumes of solute polystyrenes and it was stressed that a 10°C change in column temperature caused a decrease of about 1% in retention volume, which corresponds to an error of more than 10% in molecular weight at the same retention volume. Two main factors which cause the retention volume fluctuation were assumed to be (1) an expansion or a contraction of the mobile phase in the column due to the temperature difference between column and solvent and (2) the adsorption effects of a solute to the gel phase.

In SEC, solutes are separated according to their hydrodynamic volumes in solution. Cantow et al. [1] and Little and Pauplis [2] have explained the effect of column temperature to retention volume by the variation of polymer coil size. However, at a molecular weight of 100,000 and an increase in temperature of 115°C from 35 °C, the linear expansion coefficient of polystyrene in 1,2,4-trichlorobenzene was 1.05 [1], so that the estimated change in retention volume caused by the increase in hydrodynamic volume was about 0.07% when an increase in temperature was 10°C [3]. In the previous paper [3], it has been assumed that the estimated change in hydrodynamic volume caused by the change in column temperature was negligibly small.

However, it is obvious that temperature of a polymer solution affects its limiting viscosity number [4,5]. which increases or decreases with temperature and exhibits a maximum in an limiting viscosity number vs. temperature curve when it is measured over sufficiently wide range of temperature [5]. Because the value of hydrodynamic volume of a polymer in solution is proportional to the product of its limiting viscosity number [η] and molecular weight M, the change in limiting viscosity number with temperature will also affect the retention volume of the polymer. In other words, the evaluation of the change of the limiting viscosity number with temperature can estimate the change of the retention volume caused by the variation of the hydrodynamic volume with column temperature.

In this paper, the temperature dependence of limiting viscosity number of polystyrene dissolved in several solvents commonly used in SEC is demonstrated and the contribution to the retention volume of hydrodynamic volume fluctuation with temperature is estimated.

EXPERIMENTAL

Determination of limiting viscosity number.

Limiting viscosity number of polymer solutions in the range of concentration 0.2 - 1.0 g/dl was measured by using Ubbelohde-type viscometers (one has the range of dynamic viscosity 1.7 - 5 cst and the viscometer coefficient 0.00463 cst/s and the other 3 - 10 cst and 0.00980 cst/s). A sample polymer used for the measurement of limiting viscosity number was a commercial polystyrene ESBRITE ($\bar{M}_w = 2.87\text{x}10^5$ and $\bar{M}_n = 1.08\text{x}10^5$). Viscosity numbers of the polymer solutions were calculated by dividing the specific viscosities (which are relative viscosities minus 1) by the corresponding concentrations. The limiting viscosity number of a polymer solution was then obtained by plotting viscosity numbers vs. concentrations and by extrapolating the line to the intersection at zero concentration. Solvents used for the measurements of limiting viscosity number of polystyrene were tetrahydrofuran (THF), toluene, chloroform, cyclohexane and a benzene-methanol mixed solvent (77.8/22.2 vol/vol).

Determination of retention volume.

A Jasco (Japan Spectroscopic Co. Ltd., Hachioji, Tokyo 192, Japan) TRIROTAR high performance liquid chromatograph was used with a Shodex Model SE-11 differential refractometer (Showa Denko Co., Minato-ku, Tokyo 105, Japan). Column systems were DuPont Bimodal SEC columns (PSM-60S and PSM-1000S) packed with deactivated silica gel and two Shodex A80M SEC columns packed with polystyrene gel. Columns were thermostated at specified temperatures to an accuracy of 0.1°C in a water bath. Mobile phases were toluene, chloroform for DuPont columns and cyclohexane for Shodex columns.

Monodisperse polystyrene (PS) standards (Pressure Chemical Co., Pa., USA) were used as test samples. A portion of 0.1 ml of 0.05% polystyrene solutions was injected into columns. The flow rate of the pump dial was adjusted to 0.5 ml/min for PSM columns and 1.0 ml/min for Shodex columns and the actual flow rate was checked at the outlet of the RI detector by measuring the time required to fill a 10-ml measuring flask with solvent eluted from the system.

Measurement of peak retention volumes was performed five times and average values were obtained. These retention volumes were first taken in units of time and then calculated by multiplying the retention time by the flow rate measured at the outlet of the RI detector. The retention volume thus obtained was then corrected by subtracting or by adding the amount due to the difference between column temperature and the mobile phase temperature in the reservoir. The partition coefficient (K_{SEC}) of each polystyrene standard was calculated as follows:

$$K_{SEC} = (V_c - V_o) / V_i$$

where V_c is the corrected retention volume of a polystyrene standard, V_o the void volume or interstitial volume of gel in the columns (V_o for PSM 5.33 ml and for A80M 20 ml), and V_i inner volume of gel in the columns (V_i for PSM 4.37 ml and for A80M 21 ml).

RESULTS and DISCUSSION

The dependence of limiting viscosity number on temperature for PS (unfractionated PS) in five solvents is shown in Figures 1 and 2. In these figures, we can see that a range of temperature where

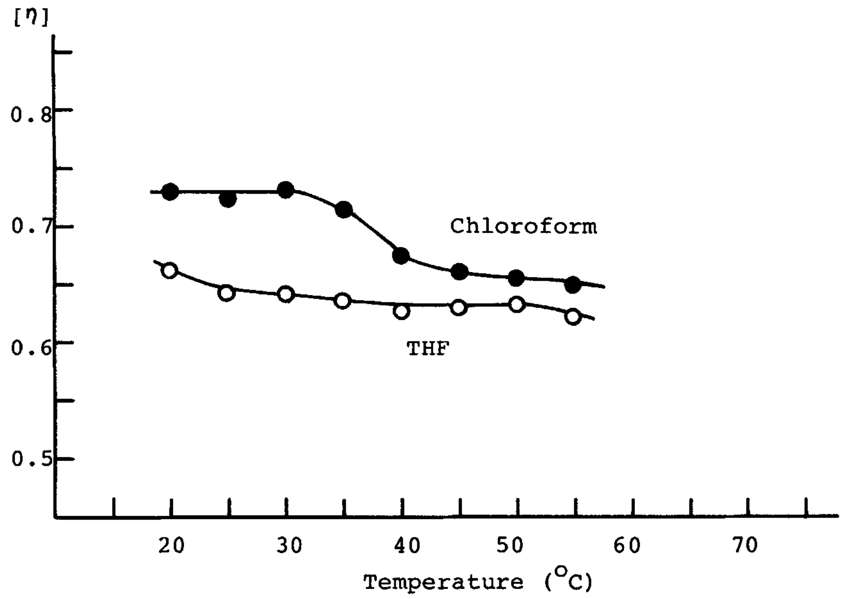

FIGURE 1. Plot of limiting viscosity number versus temperature for unfractionated polystyrene in chloroform and THF.

a variation of limiting viscosity number is below 0.01 is at 25° - 50°C for THF, 35° - 65°C for toluene, 20° - 30°C and 45° - 55°C for chloroform, and 25° - 45°C for benzene/methanol (77.8/22.2 vol/vol). In these temperature ranges, the contribution of hydrodynamic volume difference due to temperature fluctuation to retention volume would be negligible. The limiting viscosity number of PS in cyclohexane increased with increasing temperature and that in benzene/methanol increased similarly over 45°C. The mechanism of temperature dependence of limiting viscosity number is out of our scope.

In the previous paper [3], it was observed that a 10°C change in column temperature caused about a 1% shift of retention volume and resulted in errors of more than 10% in molecular weight at the same retention volume. In this experiment, a 10°C increase from 25°C for toluene or a 15°C increase from 30°C for chloroform was found to cause an about 10% increase or decrease in hydrodynamic volume of PS in these solvents, respectively, resulting in the

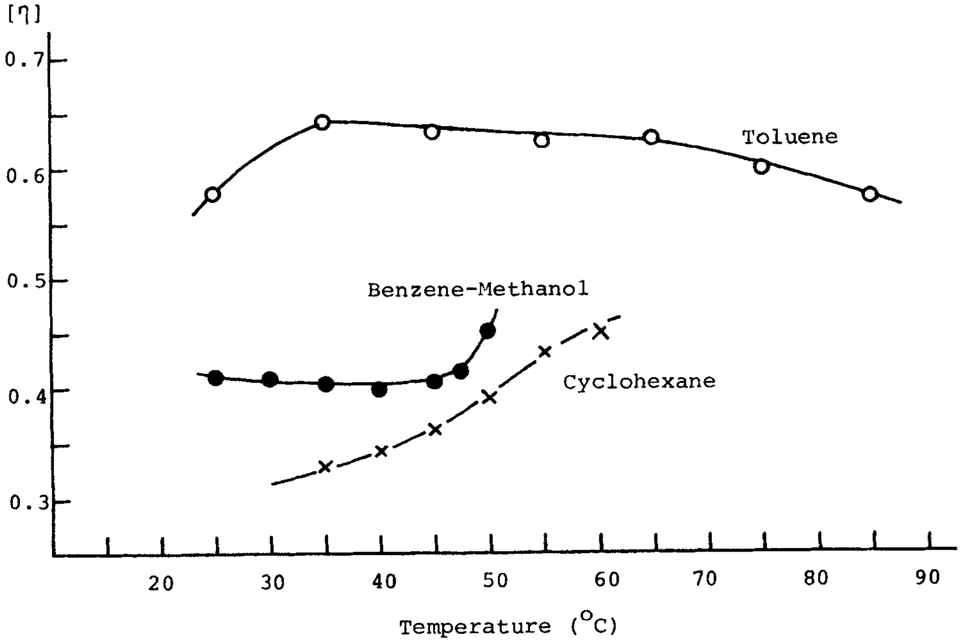

FIGURE 2. Plot of limiting viscosity number versus temperature for unfractionated polystyrene in toluene, cyclohexane and a benzene - methanol mixed solvent.

change of 0.5% in retention volume which corresponds to a 5% change in molecular weight.

A shift of retention volume with increasing column temperature will be resulted in next three main factors:

(i) An expansion of the mobile phase in the column due to the difference of temperatures between the column and a solvent reservoir (and a pumping system).

(ii) The adsorption effects of a solute to the gel phase.

(iii)A change of hydrodynamic volume of a solute.

In the previous paper [3], the third factor was excluded. In the experimental range of 25° - 45°C in the mobile phase THF, it is observed to be correct (see Figure 1). However, in the range where the limiting viscosity number fluctuates, the effect of a change of

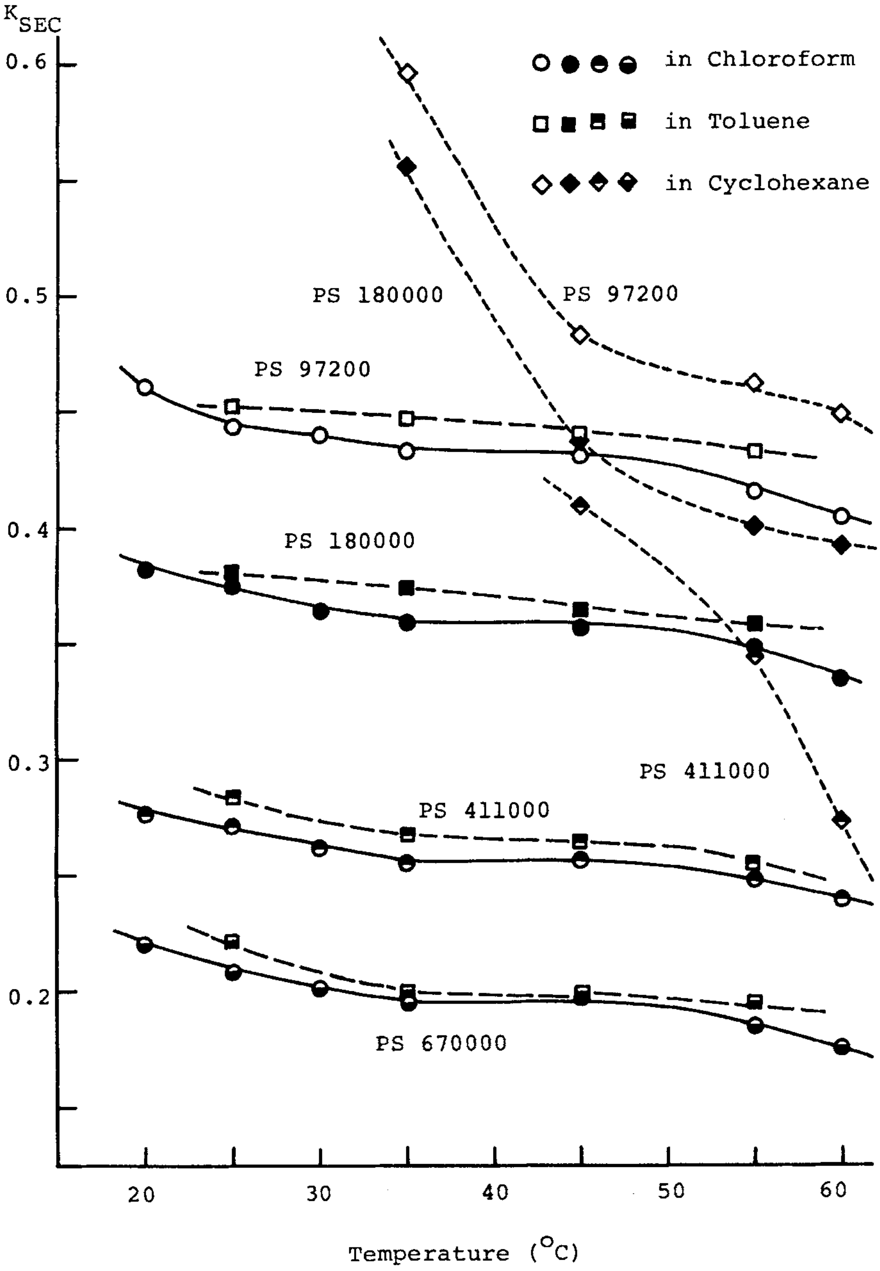

FIGURE 3. The relationship between column temperature and partition coefficients for polystyrene standards in chloroform, toluene and cyclohexane.

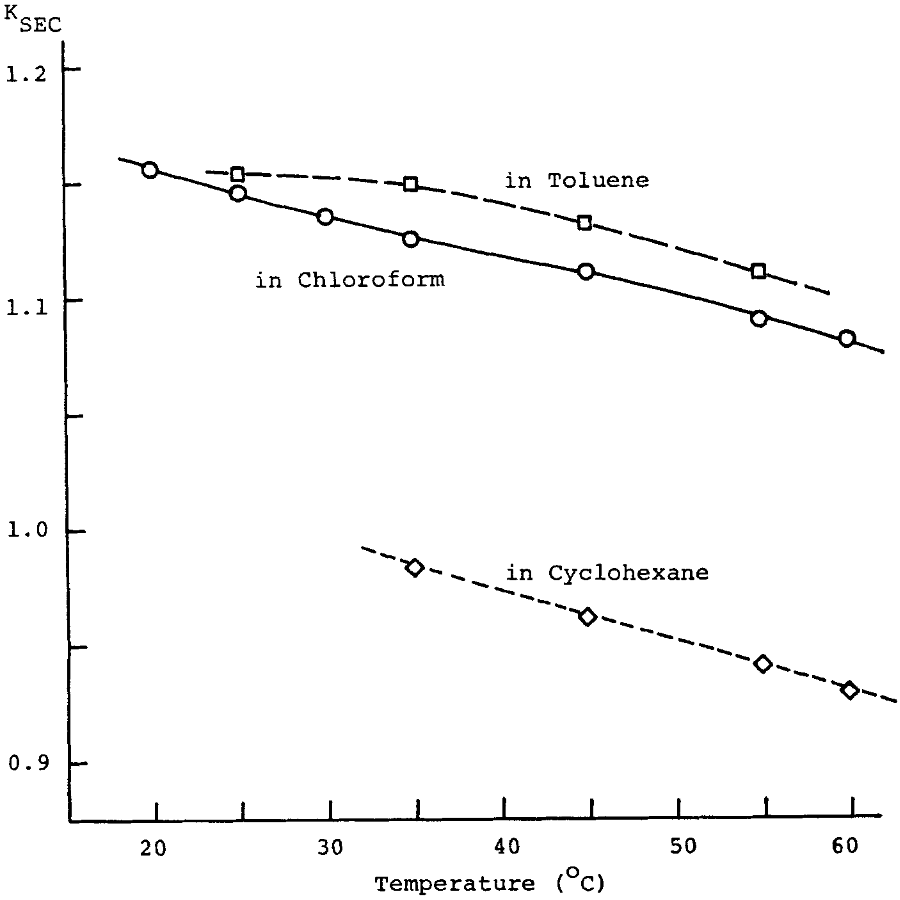

FIGURE 4. The relationship between column temperature and partition coefficients for n-hexane in chloroform, toluene and cyclohexane.

hydrodynamic volume can not be ignored. The increase in column temperature causes the expansion of the mobile phase in the column and the reduction of the adsorption effect of a solute to the gel phase, resulting in the decrease of the retention volume. On the other hand, in case of the temperature dependence of the limiting viscosity number, as shown in Figures 1 and 2, there are three types; constant over some range of temperature difference, the increase or the decrease with increasing temperature. When the limiting viscosity number increases with temperature, then the retention volume decreases, as is the case in (i) and (ii). If the limiting viscosity number decreases with increasing temperature, the retention volume will increase and result in the counterbalance to the effects of expansion of the mobile phase and of the adsorption to the gel phase. This will be the case for the range 30° - 45°C in chloroform.

Figures 3 and 4 show the relationships between column temperature and the partition coefficients K_{SEC} for four PS standards and n-hexane in three different mobile phases. In chloroform, a plateau in the curve is observed at 35° - 45°C as is expected from the above discussion.

In toluene, the deviation of the values of K_{SEC} between 25°C and 35°C is much than those between 35°C and 45°C and between 45°C and 55°C, which corresponds to the increase in the limiting viscosity number at 25°C with increasing temperature.

In cyclohexane, the values of K_{SEC} decrease significantly with increasing in temperature. This phenomena may be attributed to the increase of the limiting viscosity number with temperature in addition to the decrease of the adsorption effect with increasing in temperature.

The values of K_{SEC} for n-hexane decrease uniformly with increasing in temperature, suggesting the participation of the hydrodynamic volume effect in the temperature dependence of the values K_{SEC} of polystyrene solutes.

In conclusion, the recommended column temperature is in the range where the temperature dependence of the limiting viscosity number of polystyrene solutions is negligible; e.g., at 25° - 50°C for THF, 35° - 65°C for toluene, and 20° - 30°C and 45° - 55°C for chloroform. Column temperature in the range of 30° - 45°C in chloroform, though the temperature dependence of limiting viscosity number is significant, the counterbalance of the three effects makes the temperature dependence of the retention volume minimum. Though hydrodynamic volume or size of polymer in solution should essentially be measured by light scattering technique, our discussion would still be effective in the point of the factors that affect the reliability to a molecular weight - retention volume relationship.

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