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Evaluation of the ‘‘effective volume shift’’ method for axial dispersion corrections in multi-detector size exclusion chromatography

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Abstract

Band broadening in size exclusion chromatography (SEC) causes errors in the calculated molar mass distribution even when molar-mass-sensitive detectors are used. These errors can be partially corrected by shifting the elution volume of the molar-mass-sensitive detector chromatogram relative to the concentration detector chromatogram, and then re-calculating the molar mass distribution. In this paper a computer simulation of multi-detector SEC of a polymer with a Flory–Schulz molar mass distribution and Gaussian band broadening is used to study the volume shift method of correcting for band broadening. The results are compared with those obtained by applying a conventional band broadening correction. In the case of SEC with a light scattering detector the results from the two methods are comparable. For SEC-viscometry with universal calibration the conventional method is significantly more accurate than the volume shift method. A method for calculating the volume shift required to correct for a known amount of band broadening is also presented.

Keywords: Size exclusion chromatography; Band broadening; Molar mass distribution

1. Introduction

Size exclusion chromatography (SEC) is the primary method for measuring the molar mass and molar mass distribution of polymers. The elution volume, from the SEC column, for a monodisperse polymer with a certain molecular weight, is determined by the hydrodynamic size of the molecule in solution. For a polydisperse polymer, species with different molecular weights are separated and elute at different elution volumes. Under ideal conditions the width of the chromatographic peak reflects the width of the molar mass distribution (MMD) of the polymer. In practice, band broadening leads to a broadening of the elution profile. Band broadening in SEC is predominantly due to mass transfer between the stationary phase, which is the solvent in the pores of the packing material, and the mobile phase [1]. When the broadened elution profile is converted into a molar mass distribution using the calibration curve, the width of the molar mass distribution is overestimated.

If a molar-mass-sensitive detector, such as a light-scattering (LS) detector, is used after the chromatographic column, then the molar mass can be measured directly at each elution volume across the peak. However, as a result of band broadening, this will be an average value of the local mixture at each elution volume. In SEC-LS, the weight-average molar mass is measured at each elution volume. The total weight-average molar mass is correctly measured but the number-average molar mass for the total chromatogram is overestimated. As a result the polydispersity is underestimated and the measured distribution is narrower than the true MMD. In SEC-viscometry the intrinsic viscosity distribution (IVD) is measured directly, and then converted into the MMD using the universal calibration curve [2–5]. Band broadening causes the measured IVD to be underestimated, and this leads to a compensating overestimate in the calculated MMD [6].

The errors due to band broadening in SEC-LS or SEC-viscometry can be corrected using methods similar to those used in single detector SEC. Generally, two approaches are used: the measured curve of molar mass or intrinsic viscosity against elution volume is adjusted to correct the errors, or the true chromatogram for each detector is deconvoluted from the measured chromatogram and then used to calculate the MMD based on the true calibration curve [7].

A third approach obtains the true MMD by shifting the elution volume of one of the detector chromatograms relative to the other. A number of workers have noted the

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relationship between band broadening and the interdetector volume in multi-detector SEC [6,8–10]. When multiple detectors are used with SEC, the volume difference between the different detector cells must be taken into account before the data are analyzed, so that the measured values from each detector correspond to the same fraction of the eluting chromatogram. When molar-mass-sensitive detectors are used with SEC, the width of the calculated molar mass distribution can be changed by altering the size of the volume correction used to compensate for the dead volume between detector cells. For example, in SEC-LS the effect of band broadening is to narrow the measured molar mass distribution. If the interdetector volume is altered so that the LS peak appears to elute earlier than it actually does, then the calculated molar mass distribution is broadened. As the LS detector is generally placed before the DRI in the eluent flow, this means using a value for the interdetector volume that is lower than the true value. Conversely, if the interdetector volume is overestimated, the distribution is narrowed.

In SEC-viscometry the effect of band broadening is to broaden the measured MMD. If the interdetector volume is altered to decrease the elution volume of the viscosity chromatogram, then this narrows the calculated molar mass distribution. The direction of the required shift in the elution volume is the same as in SEC-LS even though the effect on the measured distribution is the opposite, i.e. the measured distribution is narrowed rather than broadened. This is because the overestimation of the molar mass polydispersity is a result of the underestimation of the width of the measured IVD, due to band broadening. Moving the viscometer chromatogram to a lower elution volume broadens the measured IVD and thus narrows the calculated MMD.

The errors due to band broadening can thus be approximately corrected by manipulation of the interdetector volume, rather than using a complex band broadening correction. This ''effective detector volume'' will then correct for the dead volume between detectors and simultaneously correct for band broadening [8]. In this paper, the results of a computer simulation of multi-detector size exclusion chromatography of polymers is used to evaluate the accuracy of the volume shift band broadening correction in both SEC-LS and SEC-viscometry. The calculated results are compared with the true values and with those obtained using the axial dispersion method of Netopilik [11,12] based on Tung's axial dispersion equation for conventional SEC [13–15]. This paper is the sixth in a series using computer simulation of chromatograms to study issues in SEC characterization of polymers [6,16–19].

2. Methodology

The Flory–Schulz molar mass distribution was used to generate the data [20–22],

$$F(x) = \frac{(-\ln p)^k x^{k-1} p^x}{\Gamma(k)} \quad (1)$$

where $F(x)$ is the number fraction of species of degree of polymerization x. For linear step-growth polymerization, p is the extent of the reaction and k is equal to 1. In this case, Eq. (1) reduces to the Flory most probable distribution. For addition polymerization, p is the probability of propagation steps among the combined total of propagation and termination steps. In general, $k = 1$ for termination by disproportionation and $k = 2$ for termination by second-order combination.

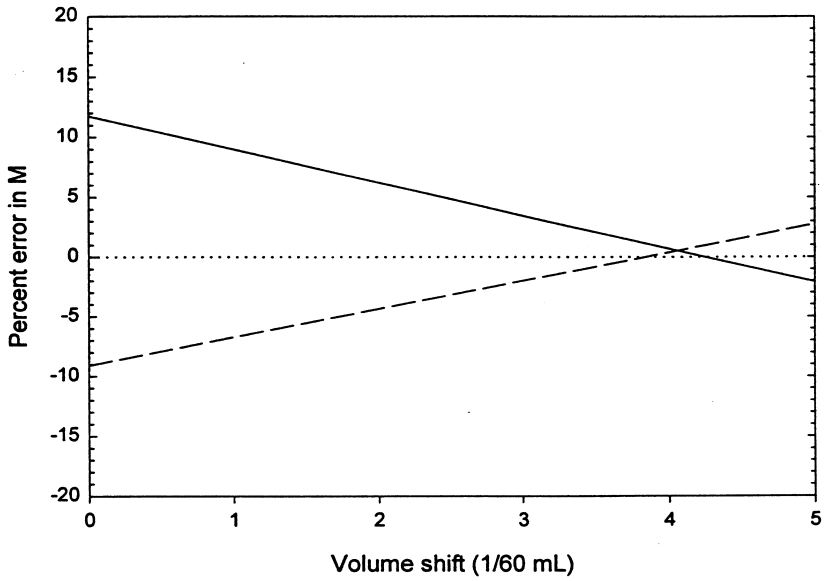

Fig. 1. Effect of shifting the elution volume of the LS chromatogram on the errors in the calculated molar mass averages, M_n (– – –), M_w (· · ·), and M_z (——), for the MMD with $\sigma = 0.4$ mL. The volume shift is shown in increments of 1/60 mL.

The SEC elution volume of each species, and the multi-detector SEC data for this molar mass distribution, were calculated using the methods described previously [6]. The concentration profile of each molecular species at elution volume point V with concentration c_i, was broadened by a Gaussian spreading function $G(V - y)$ with standard deviation σ

$$G(V-y) = \frac{c_i}{\sigma\sqrt{2\pi}} e^{-(V-y)^2/2\sigma^2} \quad (2)$$

where y represents the elution volume. The sum of these Gaussian profiles for each species in the MMD forms the concentration profile of the chromatogram. Every elution volume contains a distribution of molar masses, and the number, weight and z-averages at each volume were calculated.

For this study a series of linear molar mass distributions with a most probable distribution ($k = 1$), were generated with different amounts of band broadening ranging from none to $\sigma = 0.4$ mL. The extent of reaction was $p = 0.99$ and the repeat unit molar mass was 100 g mol^{-1}. The true molar mass averages for this distribution were $M_n = 10\,000$, $M_w = 19\,900$ and $M_z = 29\,850$ g mol^{-1}. The polydispersity indices were $M_w/M_n = 1.99$ and $M_z/M_w = 1.50$.

3. Results and discussion

3.1. Volume shift correction

3.1.1. SEC-light scattering

Initially the signals from the different detectors are aligned using the correct value of the interdetector volume (in the case of the model this is zero). The molar mass at each elution slice was calculated from the ratio of the light scattering detector and refractometer outputs at each elution volume, and the molar mass averages were calculated. Then the light scattering chromatogram was shifted one data point (equivalent to 1/60 mL) to a lower elution volume and the molar masses and averages were recalculated. These values were compared to the true values. The procedure was repeated until the results were as close to the true values as was possible. Fig. 1 shows the effect on the measured moments of the MMD of shifting the LS chromatogram to lower elution volumes. The data are for the case with band broadening of $\sigma = 0.4$ mL. Initially, M_n is overestimated by 12% and M_z is underestimated by 9%. Each shift of the chromatogram by one data point changes these values by 2–3%. Because the LS detector measures the weight-average molar mass of a polydisperse mixture at each elution slice, the total weight-average molar mass is unaffected by band broadening. In addition, shifting the LS chromatogram to another elution volume does not affect the measured weight-average molar mass, and so this value remains constant. When the LS chromatogram is shifted by four data points, equivalent to 0.067 mL, the M_n and M_z values are corrected to within a fraction of a percent of the true values. The polydispersity values are similarly corrected.

For the data with band broadening of $\sigma = 0.2$ mL, the initial error in M_n and M_z was + 5% and − 3%, respectively. A shift of one data point or 0.017 mL was required to obtain values within 1% of the true values. In both cases, agreement within 1% of the true values was obtained for the average molar masses, despite the fact that the chromatograms could only be shifted by discrete steps of 1/60 mL. When $\sigma = 0.3$ mL, a shift of 0.033 mL was required to obtain the closest values.

Fig. 2 illustrates the magnitude of the required shift in the light scattering detector elution volume to correct for the

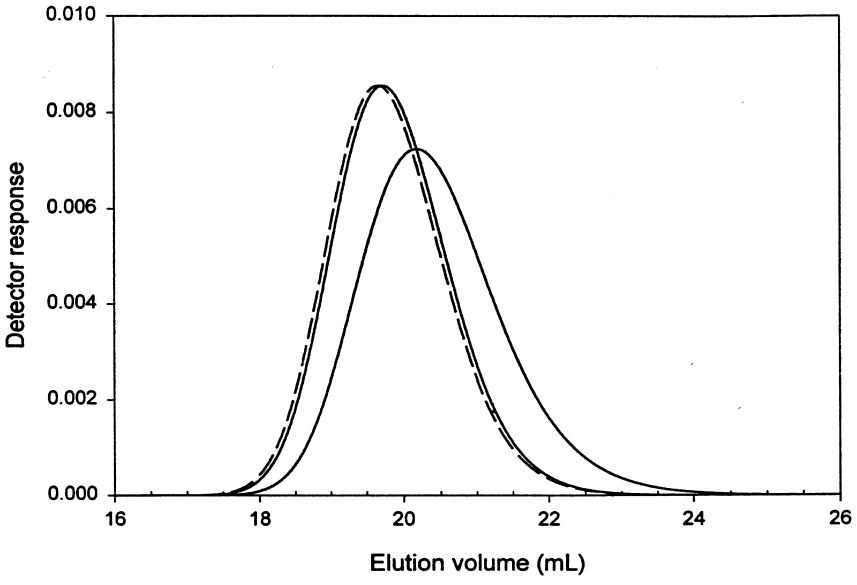

Fig. 2. RI and LS chromatograms for the model molar mass distribution with $\sigma = 0.4$ mL. The LS peak appears at lower elution volume than the RI peak due to molar mass polydispersity. The dashed line shows the LS chromatogram shifted by 0.067 mL to correct for the band broadening errors in the MMD.

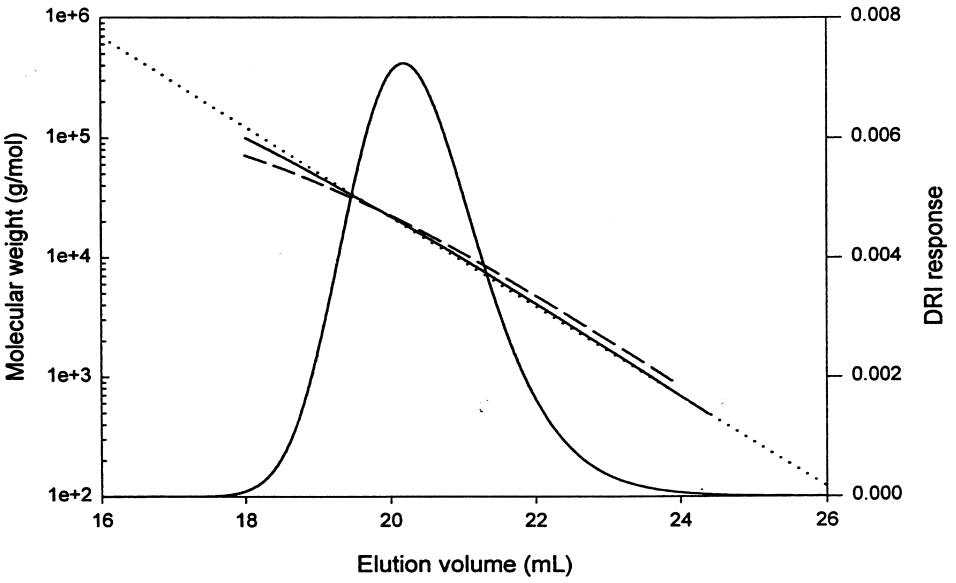

Fig. 3. The measured (– – –) and corrected (——) values of molar mass against elution volume, determined by SEC-LS for the data shown in Fig. 2. The corrected values were determined using the volume shifted LS chromatogram. The true molar mass calibration curve (· · ·) and the RI chromatogram are also shown.

band broadening. The area-normalized LS and RI chromatograms for band broadening of $\sigma = 0.4$ mL are shown. The LS chromatogram is also shown shifted by the 0.067 mL to lower elution volume required to correct for band broadening. Fig. 3 shows the RI chromatogram and the molar mass as a function of elution volume calculated from the raw data and then recalculated after shifting the LS chromatogram. In both cases the lines are curved due to the asymmetry of the Flory–Schulz distribution. The average slope of the adjusted molar mass curve is slightly less than the true calibration curve slope. This is required to compensate for the fact that the RI chromatogram used to calculate the concentration at each molar mass is still broader than the true unbroadened chromatogram.

3.1.2. SEC-viscometry

For SEC-viscometry using universal calibration to calculate the molar mass, the effect of the band broadening on the molar mass distribution is different. The calculated MMD is broader than the true MMD, and the errors are larger than the errors in SEC-LS or conventional SEC. Fig. 4 shows the errors in the calculated molar mass averages for the data set where $\sigma = 0.4$ mL. The errors in the initial results are -17% for M_n, $+15\%$ for M_w and $+62\%$ for M_z. The best

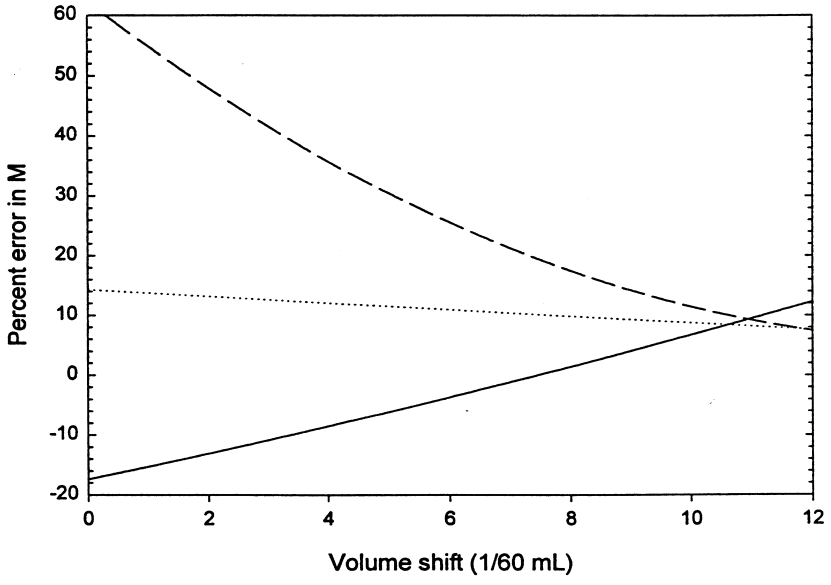

Fig. 4. Effect of shifting the elution volume of the viscometer chromatogram on the errors in the calculated molar mass averages, M_n (– – –), M_w (· · ·) and Mz (——), for the MMD with $\sigma = 0.4$ mL. The volume shift is shown in increments of 1/60 mL.

agreement with the true values was obtained by shifting the viscometer chromatogram by 10 data slices, or 0.167 mL. However, the final results are overestimated by about 10%. Further correction decreases the weight and z-average molar masses towards their true values, but increases the errors in the number-average molar mass and the polydispersities.

Fig. 5 shows the DRI chromatogram and the molar mass curves calculated from the raw data and from the volume shifted data ($\sigma = 0.4$ mL). The initial data is curved in the opposite direction from that obtained from the raw LS data because of the opposite effect that band broadening has in the case of universal calibration. The curve obtained after the volume shift correction is comparable to that in Fig. 3. Similarly, the effective volume correction does not recover the correct MHS coefficients. In this model the values were $K = 0.009$ mL/g and $a = 0.71$. With $\sigma = 0.2$ mL the measured values were $K = 0.014$ and $a = 0.65$ and the corrected values were $K = 0.010$ and $a = 0.70$. For $\sigma = 0.4$ mL the measured values were $K = 0.034$ and $a = 0.56$ and the corrected values were $K = 0.013$ and $a = 0.66$.

The reason for the errors is that, although the correct IVD can be approximated by shifting the elution volume of the viscometer chromatogram, the calculated intrinsic viscosity values are shifted in elution volume relative to the calibration curve. When the universal calibration curve is then used to convert the IVD into the MMD this shift relative to the calibration curve leads to the errors. The viscometer is shifted to lower elution volumes, corresponding to higher values of hydrodynamic volume on the universal calibration curve. As a result the molar mass at each elution volume is overestimated. In SEC-LS the calibration curve is not used, so the shift does not lead to these errors. One solution is to shift the RI chromatogram in the opposite direction, towards higher elution volumes. For a symmetrical Gaussian peak, shifting the two detectors equally in opposite directions would lead to the correct molar mass averages. In this case, as a result of the peak asymmetry, the best results were found by shifting the viscometer by seven data slices and the viscometer by three slices, retaining the total relative shift of 10 data points. This shift gave $M_n = 9900$, $M_w = 20\,000$, $M_z = 30\,400$ and $M_w/M_n = 2.02$.

3.2. Correction using Tung's axial dispersion equation

In this section the results obtained using the volume shift correction are compared with results obtained by using a band broadening correction procedure based on Tung's axial dispersion equation, extended to multi-detector SEC by Netopilik [11]. Once the true chromatograms for each detector have been recovered, the molar mass distribution can be determined, either by calculating the molar mass directly from the light scattering detector response, or by using the viscometer response and the universal calibration curve.

Fig. 6 shows the measured and corrected chromatograms for the LS and RI detectors. In both SEC-LS and SEC-viscometry the corrected molar mass averages were within 2% of the true values, and in most cases the errors were less than 1%. In addition the MHS parameters obtained by universal calibration were correct. Fig. 7 shows the molar mass curves for the measured and corrected data obtained by SEC-LS. In this case the slope of the corrected data is the same as the true calibration curve, because the RI chromatogram has been corrected for band broadening. Fig. 8 shows similar data for SEC-viscometry.

3.3. Calculation of the ''effective interdetector volume'' shift

The model of the log normal molar mass distribution can be used to derive an expression to calculate the effective

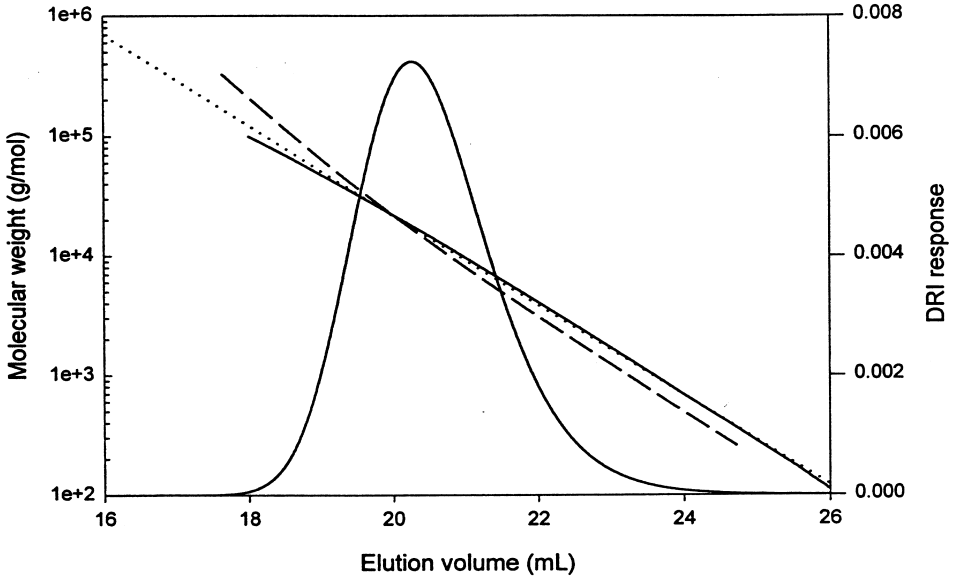

Fig. 5. The measured (– – –) and corrected (——) values of molar mass against elution volume, determined by SEC-viscometry for the data shown in Fig. 2. The corrected values were determined using the volume shifted viscometer chromatogram. The true molar mass calibration curve (· · ·) and the RI chromatogram are also shown.

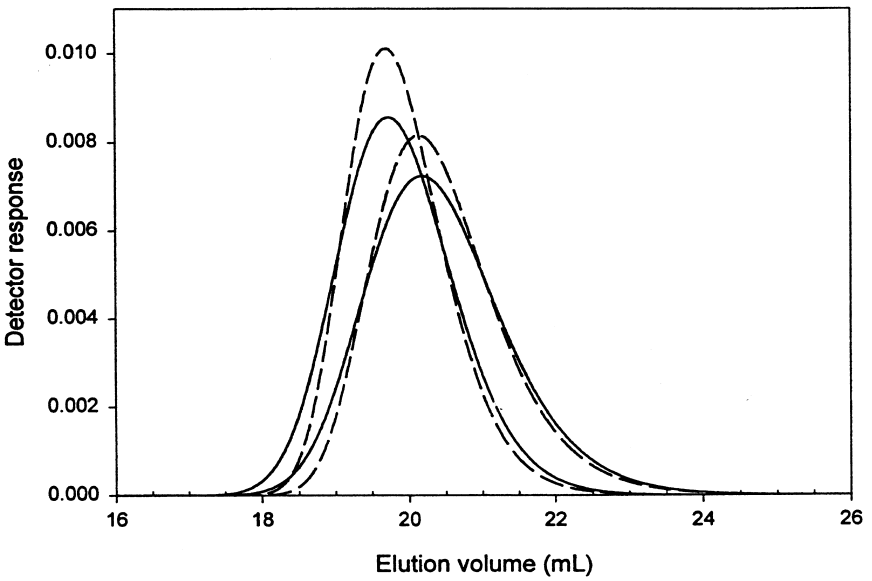

Fig. 6. RI and LS chromatograms for the model molar mass distribution with $\sigma = 0.4$ mL. The LS peak appears at lower elution volume than the RI peak due to molar mass polydispersity. The dashed lines show the two chromatograms after band broadening correction following the procedure described in the text.

shift in volume needed to correct for a given amount of Gaussian band broadening σ_B [6]. The polydispersity, $P = M_w/M_n$, of the log normal MMD in the ideal case without any band broadening, is related to the slope of the calibration curve D_2 and the width of the chromatogram, σ_V, in units of elution volume by

$$P = \exp\left(D_2^2\sigma_V^2\right) \tag{3}$$

The peak of the light scattering chromatogram elutes at a lower elution volume, V_{LS}, than the peak in the concentration chromatogram, V_{RI}, so $V_{RI} > V_{LS}$, and this volume difference depends only on the polydispersity of the polymer and the slope of the calibration curve

$$V_{RI} - V_{LS} = \sigma_V^2 D_2 \tag{4}$$

If the peak is for a monodisperse species then there is no shift, and the LS and RI peaks overlay each other. Gaussian band broadening, σ_B, changes the chromatogram peak width and the slope of the effective calibration curve measured by the LS detector, but not the volume difference between the LS and RI peaks. The peak width is increased to σ_T^2, where $\sigma_T^2 = \sigma_V^2 + \sigma_B^2$, and the slope of the calibration curve is related to the true calibration

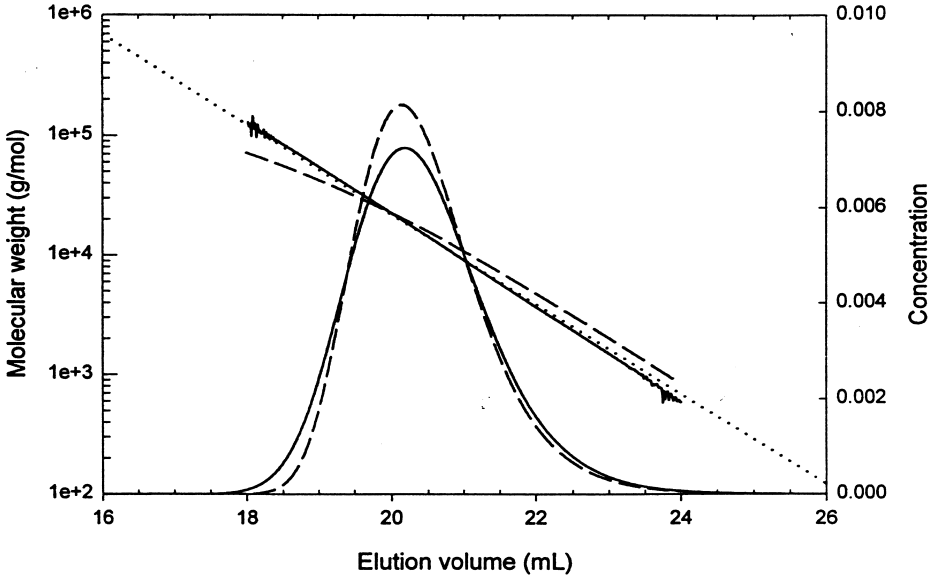

Fig. 7. The measured (– – –) and corrected (——) values of molar mass against elution volume, determined by SEC-LS for the data shown in Fig. 2. The corrected values were determined using the band broadening correction based on Tung's axial dispersion equation. Compare with Fig. 3. The true molar mass calibration curve (· · ·) and the RI chromatogram are also shown.

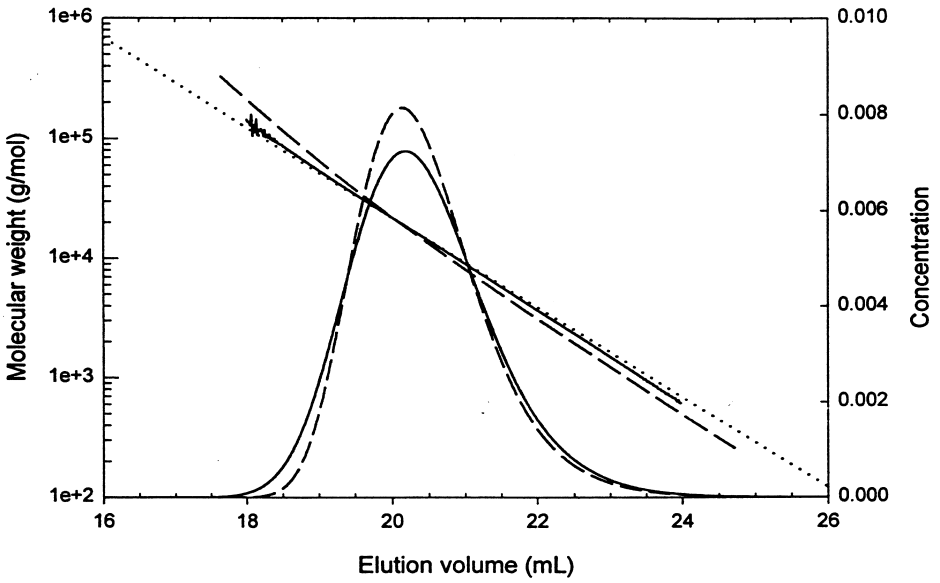

Fig. 8. The measured (– – –) and corrected (——) values of molar mass against elution volume, determined by SEC-viscometry for the data shown in Fig. 2. The corrected values were determined using the band broadening correction based on Tung's axial dispersion equation. Compare with Fig. 5. The true molar mass calibration curve (· · ·) and the RI chromatogram are also shown.

curve by

$$D_2' = \left(\frac{\sigma_V}{\sigma_T}\right)^2 D_2 \tag{5}$$

When there is band broadening, $\sigma_T > \sigma_V$, and the slope is smaller than the true slope. The polydispersity measured by the LS detector, P′, is then given by

$$P' = \exp\left(\left(D'_2\sigma_T\right)^2\right) \tag{6}$$

To correct for band broadening by shifting the elution volume of the LS peak, we need to move the peak so that the measured polydispersity P'' is equal to the true polydispersity P. This shift will change the slope of the apparent calibration curve to D''_2 so that (from Eq. (3))

$$D_2''\sigma_T = D_2\sigma_V \tag{7}$$

Comparing Eq. (7) with Eq. (5) shows that the slope of the adjusted calibration curve will be less than the slope of the true calibration curve, but greater than the slope of the measured calibration curve. The volume between the detectors must be shifted so that (from Eq. (4))

$$V_{RI} - V_{LS}' = \sigma_T^2 D_2'' \tag{8}$$

This corresponds to a shift in the elution volume of the LS

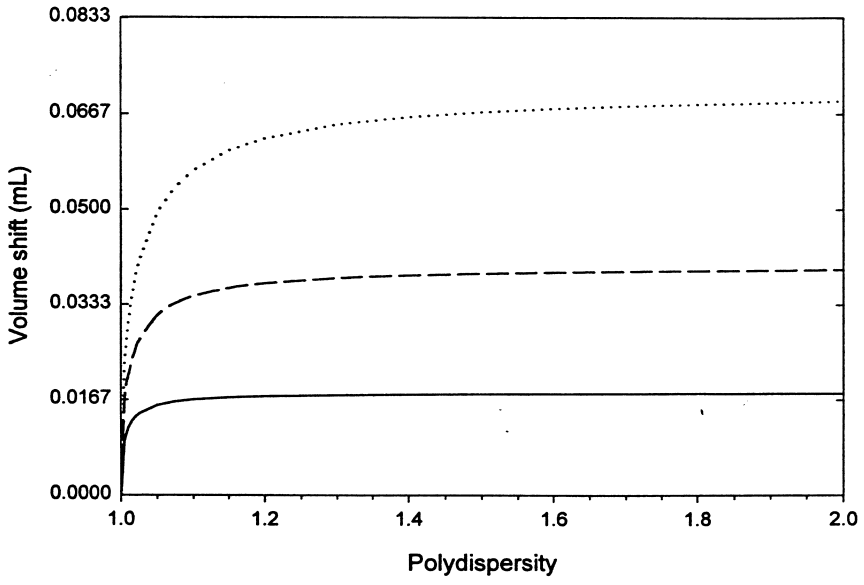

Fig. 9. The relationship between polydispersity and the volume shift required to correct for three different levels of band broadening (Eq. (2)), σ_B=0.2 (——), σ_B=0.3 (– – –), and σ_B=0.4 (· · ·) mL. The required volume shift varies with polydispersity for narrow MMDs.

detector of

$$V_{LS} - V_{LS}' = (\sigma_T - \sigma_V)\sigma_V D_2 \quad (9)$$

The required volume shift depends on the amount of band broadening and the slope of the calibration curve. In addition it depends on the polydispersity of the polymer MMD. Fig. 9 shows a plot of the required volume shift for different amounts of band broadening as a function of polydispersity. The required shift for a given σ_B is fairly constant above a polydispersity of 1.2, however below this polydispersity the shift rapidly decreases with decreasing polydispersity. For a pure monodisperse polymer no volume shift is required to correct for band broadening as expected. Although this equation is for a log normal MMD the results are in good agreement with the results obtained from the computer model of a most probable distribution. In the computer model the slope of the calibration curve D_2 is 0.9, so for a polydispersity of 2, σ_V is 0.925 (assuming Eq. (3) is a valid approximation). From Eq. (9) this gives volume shifts of 0.017, 0.038 and 0.069 mL for $\sigma = 0.2$, 0.3 and 0.4 mL, respectively, in good agreement with the results above.

4. Conclusions

A computer simulation of multi-detector SEC has been used to evaluate the accuracy of using a volume shift of the chromatogram from one detector relative to another to correct for band broadening. The results were compared with those obtained using an axial dispersion correction based on Tung's axial dispersion equation. For SEC-LS and SEC-Visc-LS the results from the two methods were comparable and the calculated molar mass averages were within 1% of the true values. For SEC-viscometry with universal calibration the volume shift method gave results with significant errors, whereas the axial dispersion correction gave accurate values. In particular, the errors in the measured MHS coefficients using the volume shift method were extremely high. The axial dispersion correction recovered the true values. The SEC-viscometry results could be improved by shifting both the refractometer and the viscometer in opposite directions in an attempt to maintain the same average elution volume. However, this level of data manipulation seems inadvisable in practice. A calculation based on the log normal MMD showed that it was possible to calculate the volume shift required to correct for a given amount of band broadening. However, the volume shift required depends on the polymer polydispersity as well as the band broadening. For polydispersities less than 1.2, the dependence is significant. This agrees with experimental evidence that the volume shift method cannot be applied to both broad and narrow molar mass distributions.

Finally, this analysis has been concerned with modeling band broadening in the SEC experiment. In practice some other factors need to be taken into consideration. Experimental noise has not been considered in this study, but it can be expected to increase the errors in both cases. The situation is further complicated by the fact that flow-rate fluctuations in the chromatograph, caused, for example, by flow restrictions, such as narrow capillaries, combined with splits in the eluent flow or excessive pulse dampening, can also lead to apparent volume shifts in the elution profile measured by a viscometer.

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