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ORIGINAL PAPER

Sedimentation studies of bi-component polystyrene solutions in analytical ultracentrifugation by comparison of two analysis methods: effect of polymer mixing ratios

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Abstract Two data analysis programs of Sedfit and VelXLAI associated with analytical ultracentrifugation were compared with each other for the sedimentation analysis of a pure polystyrene polymer solution as well as solutions of polymer mixtures in organic solvent containing two components in different mixing ratios. Interference detection optics was used for the sedimentation analysis. The pure polymer showed concentration dependency of the sedimentation coefficient and the results were similar in both the programs. In the mixture samples, slight differences in the peak sedimentation coefficients of the two polymers fractions in the analysis programs were observed. However, VelXLAI program was observed to detect the relative fractions of the two mixture components more accurately than Sedfit.

Keywords VelXLAI · Sedfit · Sedimentation · Ultracentrifugation · Mixture

Introduction

For decades, analytical ultracentrifugation has been used for colloid characterization. High statistical capability and versatility associated with analytical ultracentrifugation make it a method of choice to analyze a wide spectrum of polymer systems [1–5]. Various detection optics like turbidity, interference, absorption and

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Schlieren can be used depending on the nature of the sample to be analyzed. By using these detectors, the sedimentation of the particles or dissolved macromolecules according to their size or density can be monitored owing to the generated radial concentration gradient as a function of time. Accordingly, a number of data analysis programs also exist to convert the sedimentation data from the detector into sedimentation coefficient distributions and subsequently into particle size or molecular weight information. One of the methods which is free from any model assumptions is Gosting Fujita Lechner method (incorporated into analysis program of VelXLAI). The sedimentation coefficient distribution $g(S, C, t)$ is determined according to [6–9]:

$$S(C,t) = (\mathrm{d}r/\mathrm{d}t)/(\omega^2 r) = (1/\omega^2)\ \mathrm{d}\ln r/\mathrm{d}t = \ln(r/r_\mathrm{m})/\left(\int \omega^2 \mathrm{d}t\right)$$

$$g(S,C,t) = (1/C_0)\,[\mathrm{d}C(r,t)/\mathrm{d}r](r/r_\mathrm{m})^2 r \int \omega^2 \mathrm{d}t,$$

where C_0 is the initial concentration of the particles, $C(r, t)$ is the concentration at distance r and running time t, r is the distance from the axis of rotation, r_m is the distance of the meniscus from the axis of rotation, and $\omega = 2\pi N =$ angular velocity. The details on the method have also been provided elsewhere [10, 11].

Another widely used method which is based on a boundary model approach for sedimentation is Sedfit. It is based on generating numerical solutions to the Lamm equation [12–15] and requires the assumptions of sedimentation coefficient, frictional coefficient, and the partial specific volume for the solute. This information is required to generate finite element solutions for a large number of species with varying s values. The analysis is followed by the adjustment of the generated solutions to experimental data by maximum entropy regularization, which generates a sedimentation coefficient distribution $g(s)$. More details have also been reported in earlier studies [10, 11].

In a previous study [16], the strengths and limitations of abovementioned data analysis programs of Sedfit and VelXLAI were compared with each other in the interference optics detection mode as a function of polymer concentration. This study deals with the similar comparisons mainly for a polymer mixture, where the components are mixed in different weight ratios without changing the concentration. One component of the mixture was also analyzed in pure as a function of concentration. To achieve this, sedimentation coefficient distributions were compared in both the data analysis programs along with relative amounts of the components of the polymer mixture detected in these programs as a function of polymer mixing ratios.

Materials and methods

Polystyrene standard samples with molecular weights in the range of ~80,000 and ~670,000 g/mol were commercially procured. These samples were, respectively, designated as PS-1 and PS-2. Solutions of pure polymer as well as polymer mixture samples were obtained in methylethylketone (MEK). The details of the sedimentation velocity experiments in the interference detection optics are already described in an earlier study [16]. OPTIMA XL-I analytical ultracentrifuge from Beckman Coulter (temperature 25 °C, wavelength 675 nm) was used for the sedimentation analysis. The samples were rotated at a speed of 40,000 rotations per minute and a scan time interval of 10 s was used. Pure PS-1 polymer was measured at different concentrations ranging from ~1 to ~5 g/L, whereas polymer mixtures with PS-1 and PS-2 in the weight ratios of 100% PS-1, 90% PS-1:10% PS-2, 70% PS-1:30/ PS-2, 50% PS-1:50% PS-2, 30% PS-1:70% PS-2, 10% PS-1:90% PS-2, 100% PS-2 were used. A d*n*/d*c* value of 0.21 cm^3/g was measured for the polymer samples in the Bellingham refractometer. Sedfit and Gosting Fujita Lechner (GFL) or VelXLAI methods were used to analyze the sedimentation velocity data obtained from the analytical ultracentrifuge. The details on the method parameters for obtaining the distributions can be found elsewhere [11, 16].

Results and discussion

Accurate characterization of the amount of the different components in a mixture is generally required from a data analysis program as such information is required to be related to the performance of the materials. Similarly, the characterization of molecular characteristics of either the pure polymers or components in polymer mixtures is also required. These molecular characteristics can be directly derived from the sedimentation coefficient distributions of the materials, thus, peak sedimentation coefficient and its distribution become most important parameters for the data analysis programs. Similar to the previous study [16], where the concentration effects of polymer mixture samples were analyzed, this study also compares the Sedfit and VelXLAI data analysis methods associated with analytical ultracentrifuge to characterize mainly the effect of different mixing ratios of polymer components in a mixture while keeping the polymer concentration constant. Apart from that, a component of the polymer mixture was also measured alone as a function of polymer concentration and the observations from the two analysis methods were correlated with the results from the mixture samples.

Figure 1 shows the differential and cumulative sedimentation coefficient distributions for the polymer sample PS-1 as a function of polymer concentration when analyzed with VelXLAI program. As observed in earlier studies for both interference as well as Schlieren optics that the sedimentation coefficient had concentration dependency [16, 17]. The sedimentation coefficient distributions shifted to lower sedimentation coefficient values as a function of concentration. Polymer concentrations of 1.1, 2.1, 3.0, 4.1, and 4.9 g/L were used and the peak sedimentation coefficient for these polymer concentrations was observed to be 7.48, 7.24, 7.09, 6.85, and 6.69 Sved, respectively. Also, as observed earlier, the distributions became slightly narrower on increasing polymer concentration. The sedimentation data for the polymer sample PS-1 was also analyzed with Sedfit program for comparison and Fig. 2 shows the differential and cumulative sedimentation coefficient distributions at the same concentrations as shown in Fig. 1. The presence of single distribution confirmed the presence of one family of polymer chains and the concentration dependency of the sedimentation coefficient

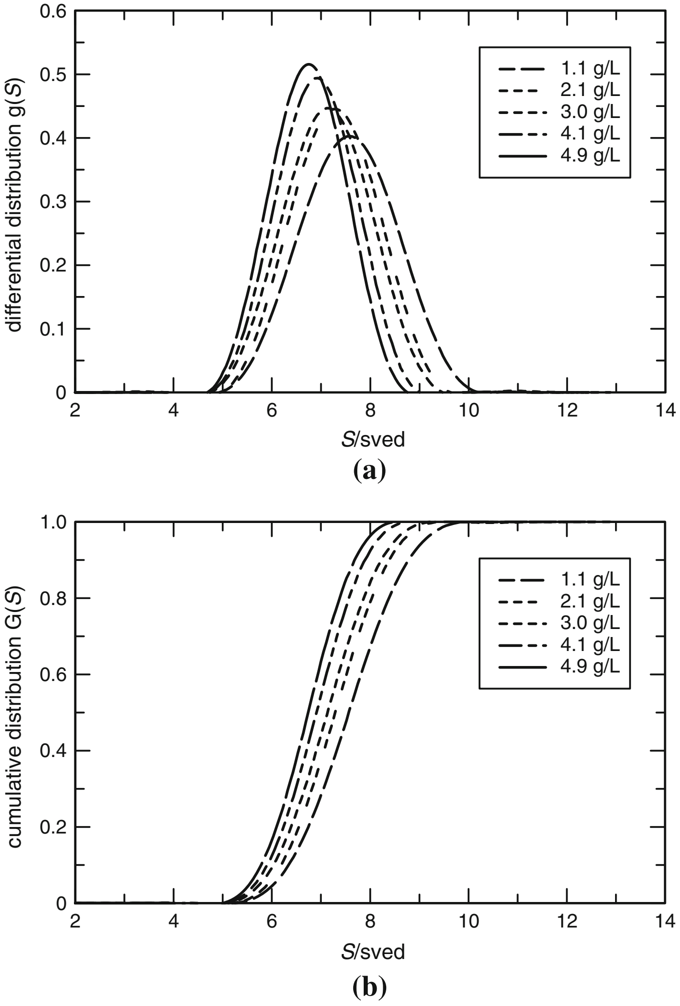


Fig. 1 **a** Differential and **b** cumulative sedimentation coefficient distributions of PS-1 at different polymer concentrations using interference detection optics and VelXLAI data analysis program

was also further confirmed. The peak sedimentation coefficient values as a function of increasing polymer concentration in Sedfit analysis were observed to be 7.65, 7.30, 7.10, 6.94, and 6.74 Sved, respectively. These values were close to the peak sedimentation coefficient values observed by the VelXLAI program. The distributions in the case of Sedfit program were in general broader than VelXLAI analysis and slight tailing at both lower and higher end of the sedimentation coefficient distributions was also observed in Sedfit analysis, however, this tailing was not a function of the polymer concentration. Figure 3 also shows the peak sedimentation coefficient values observed in both the analysis programs plotted as a function of polymer concentration. The close proximity of sedimentation coefficients at

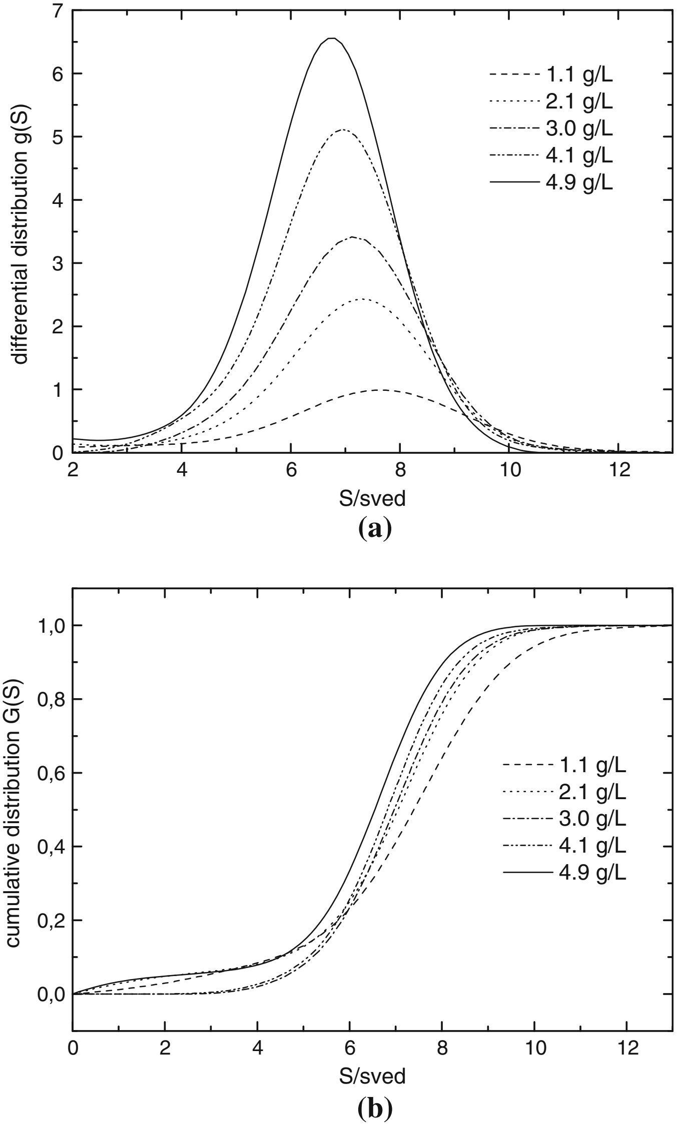


Fig. 2 **a** Differential and **b** cumulative sedimentation coefficient distributions of PS-1 at different polymer concentrations using interference detection optics and Sedfit data analysis program

different polymer concentrations for both the programs confirmed similar results from these programs for the sedimentation analysis of single component polymer solutions. Similar results were also obtained in the earlier study [16] for the pure polymer sample with molecular weight of ~350,000 g/mol, but it was also required to confirm these observations for another polymer sample, preferably with a lower molecular weight, to ascertain the effect of molecular weight on the sedimentation analysis of the single component polymer samples by the two analysis programs.

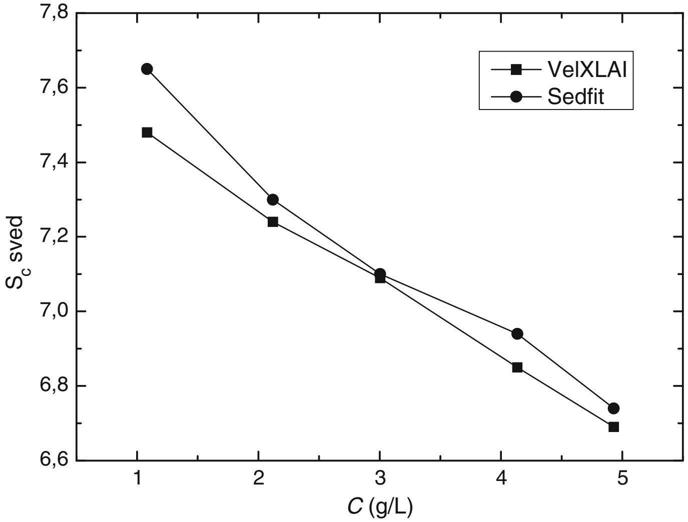


Fig. 3 Correlation of sedimentation coefficient with the polymer concentration in different analysis programs

In the previous study [16], a bi-component polymer mixture was analyzed as a function of polymer concentration to compare the analysis programs for mixture samples. In this study, the polymer concentration in the mixture has been kept constant for the comparison of the analysis methods, whereas the relative amount of two components in the mixture has been varied. Figure 4 shows the raw sedimentation profiles of the polymer mixture samples as a function of the cell radius and sedimentation time at mixing ratios of 30% PS-1:70% PS-2 and 50% PS-1:50% PS-2, respectively. The presence of two sedimentation plateaus in both the cases indicated the presence of two families of polymer chains. The scans in the sedimentation plateau corresponding to low molecular weight polymer PS-1 were observed to be more flat or sagging in nature with lower slope as compared to the scans of polymer PS-2, where a steep slope of the scans was observed. It thus qualitatively indicated that the chains in PS-1 may have a more polydisperse nature than the chains in PS-2.

Differential and cumulative distributions of sedimentation coefficient of the PS-1 and PS-2 polymer mixtures at a polymer concentration of 2 g/L when analyzed with VelXLAI program are shown in Fig. 5. The various mixtures used for the analysis were 100% PS-1, 90% PS-1:10% PS-2, 70% PS-1:30% PS-2, 50% PS-1:50% PS-2, 30% PS-1:70% PS-2, 10% PS-1:90% PS-2, and 100% PS-2. The two distributions corresponding to the two polymers were clearly separated from each other. The mixture curves touched the *x*-axis at their intersection exhibiting a clear separation between the two components. The sedimentation coefficient distributions of the PS-1 component were observed to be broader in nature as compared to PS-2 fraction confirming the observation from the raw sedimentation data. This was also further confirmed by the cumulative distribution analysis of the sedimentation coefficient as the curves corresponding to the PS-1 polymer fraction were more flat in nature,

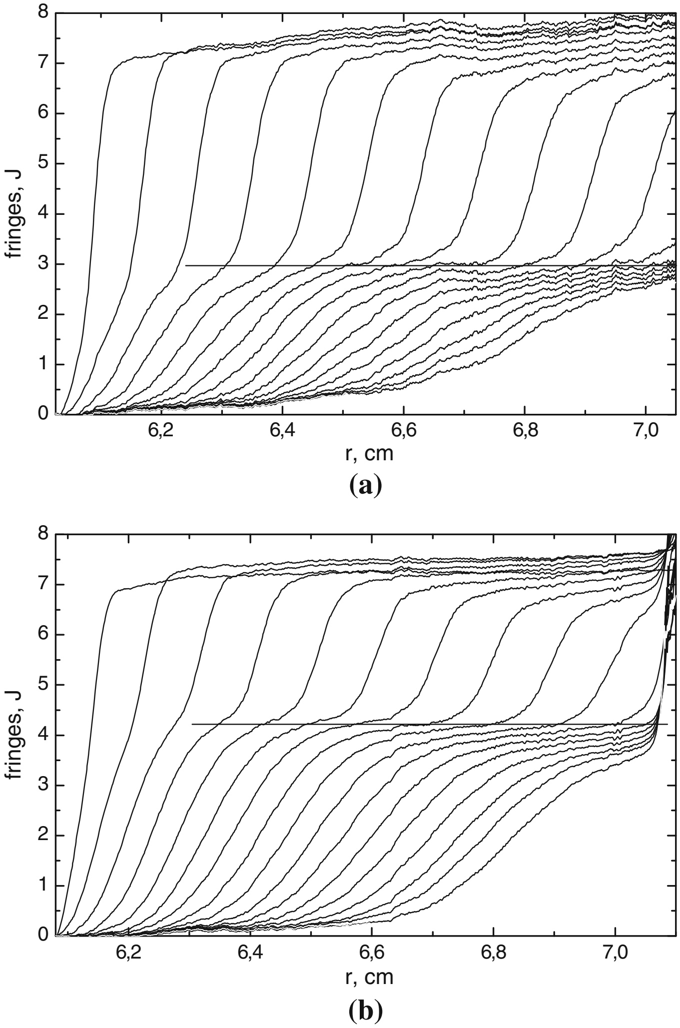


Fig. 4 Raw sedimentation profiles of PS-1 and PS-2 mixtures: **a** 30% PS-1, 70% PS-2 and **b** 50% PS-1, 50% PS-2

whereas the curves corresponding to the PS-2 fraction had steeper slope. The peak intensity of the fractions in the differential distributions increased on increasing the extent of these components in the mixture. In the cumulative distributions of the sedimentation coefficient, only single sedimentation plateaus were observed for the pure polymer fractions, whereas in other cases, two sedimentation plateaus were observed. Figure 6 similarly describes the differential and cumulative sedimentation coefficient distributions of the same mixture samples when analyzed with Sedfit program. Bimodal distributions, with PS-1 distributions more broad in nature, were observed similar to the case of VelXLAI. Thus, both analysis programs detected the two polymer fractions in the mixture at different mixing ratios; however, it is of

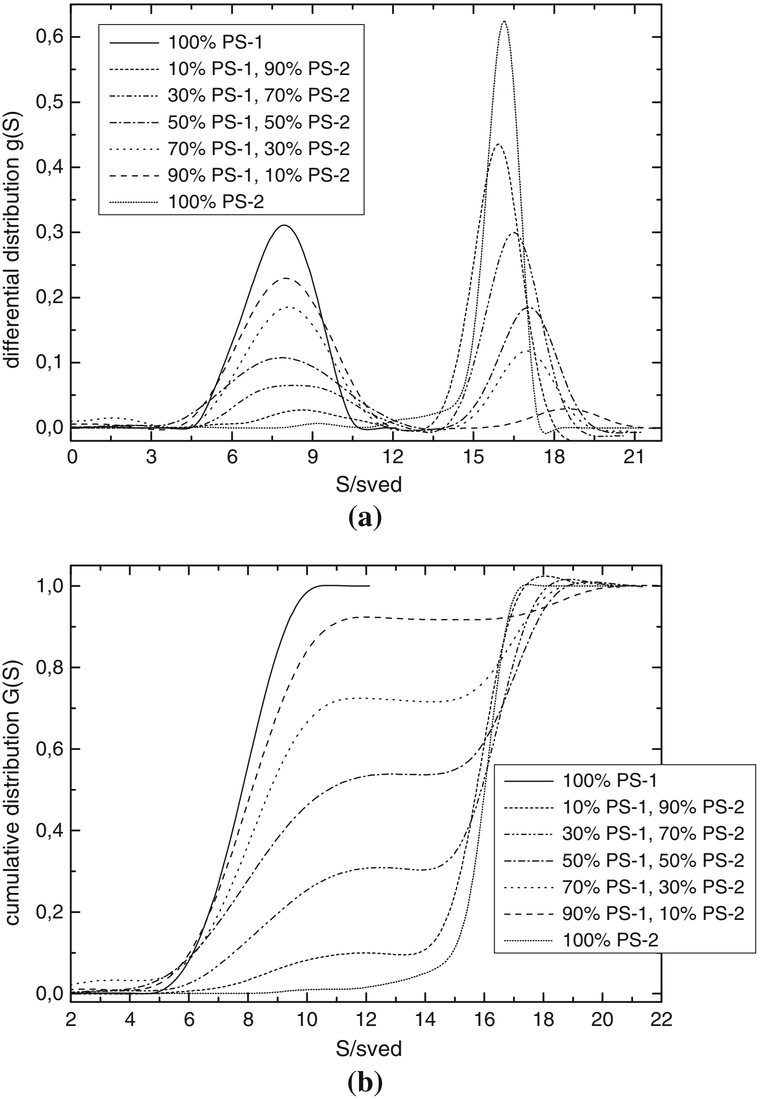


Fig. 5 **a** Differential and **b** cumulative sedimentation coefficient distributions of polymer mixtures at different mixing ratios (same polymer concentration) analyzed using VelXLAI program

interest to compare the performance of the two programs with each other in accurately determining the relative amount of fractions of the mixture.

Figure 7 shows the comparison between the analysis programs of VelXLAI and Sedfit for a mixture sample containing 50% PS-1 and 50% PS-2. Both differential and cumulative sedimentation coefficient distributions have been depicted. Though the differential distributions are very similar in both the cases, a slight shift of the distribution to higher sedimentation coefficient values was observed in the case of

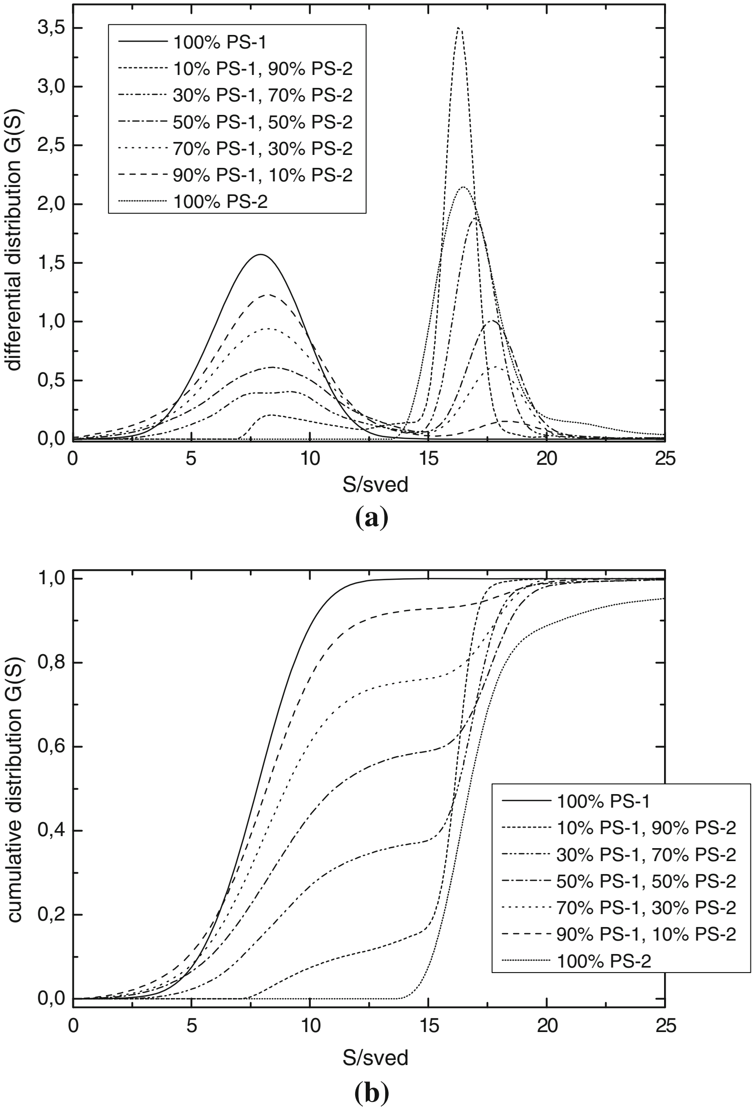
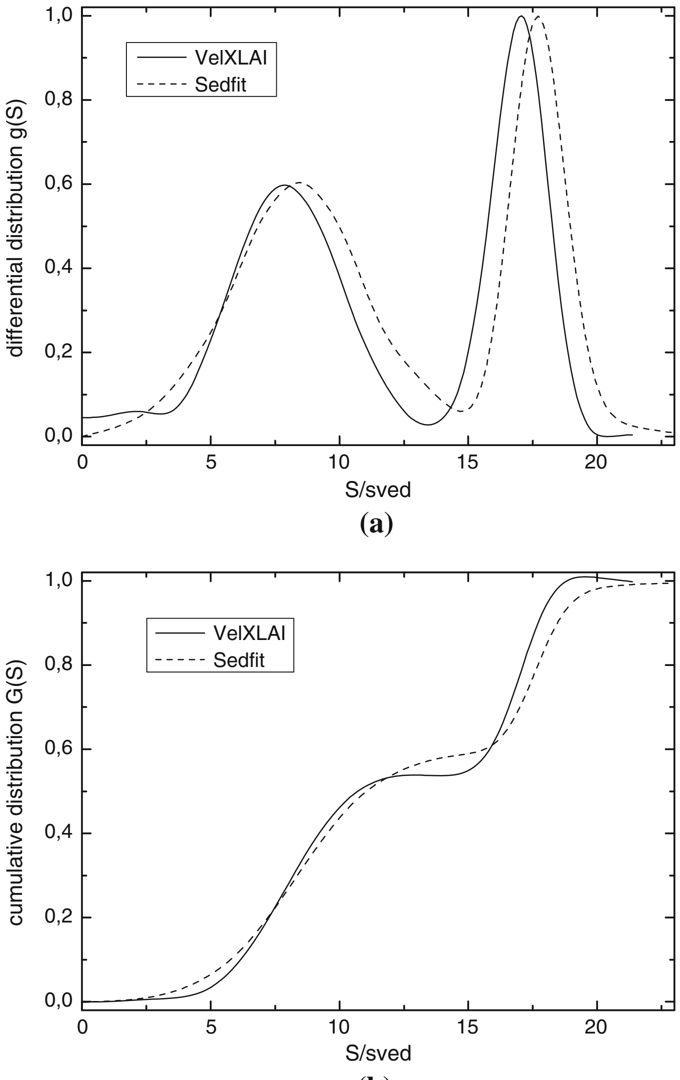


Fig. 6 **a** Differential and **b** cumulative sedimentation coefficient distributions of polymer mixtures at different mixing ratios (same polymer concentration) analyzed using Sedfit program

Sedfit analysis. More significant differences were observed in the cumulative sedimentation coefficient distributions from the two programs. The amount of PS-1 fraction detected by Sedfit analysis was 58.5%, thus significantly higher than the actual 50%. In the case of VelXLAI, the detected amount of 54% was also higher than the actual, but it was more accurate than the Sedfit analysis.

Figure 8 shows the amounts of PS-1 and PS-2 fractions in the mixture samples detected by Sedfit and VelXLAI programs as a function of ideal concentration of the

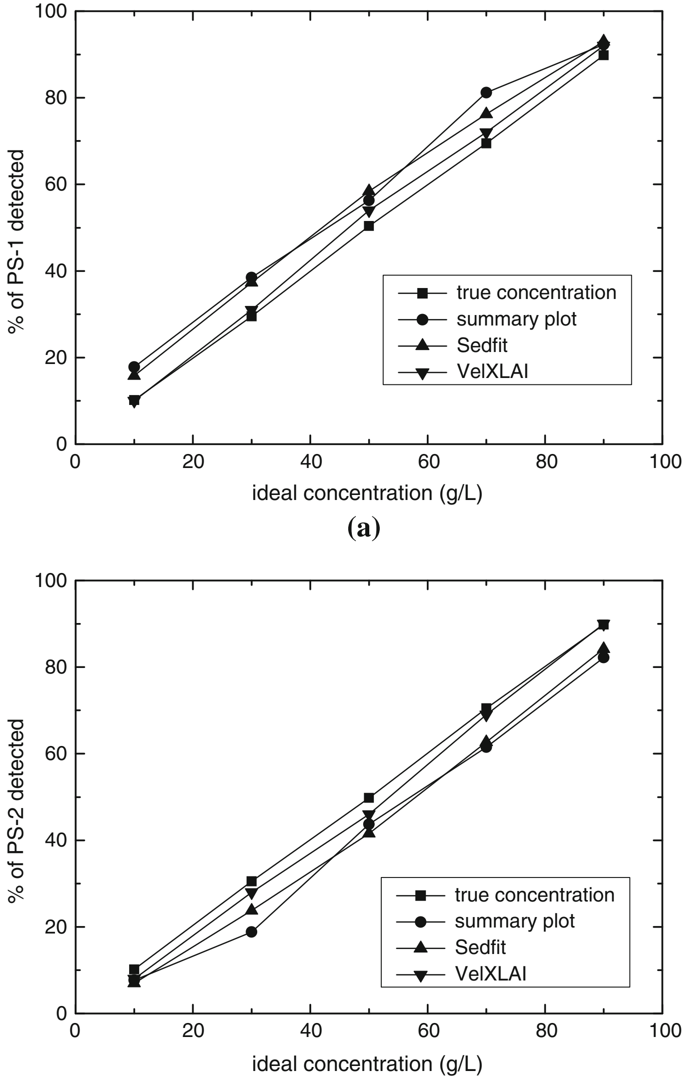


(a)

(b)

Fig. 7 Comparison of VelXLAI and Sedfit programs for a polymer mixture consisting of 50% PS-1 and 50% PS-2

polymer components in the mixture (i.e., 100% PS-1, 90% PS-1:10% PS-2, 70% PS-1:30% PS-2, 50% PS-1:50% PS-2, 30% PS-1:70% PS-2, 10% PS-1:90% PS-2, and 100% PS-2). The true concentration, which corresponds to the ideal concentration, is also plotted for comparison. The values from the summary plot (i.e., from the raw sedimentation data) have also been plotted. For the ideal values of 10, 30, 50, 70, and 90% PS-1, the values of 15.8, 37.3, 58.5, 76.2, and 93.0% were observed in the Sedfit analysis. Similarly, for the ideal values of 10, 30, 50, 70,



(a)

(b)

Fig. 8 Correlations of amount of polymer fractions detected using different analysis programs as a function of mixture composition

and 90% PS-1, the values of 10.0, 31.0, 54.0, 72.0, and 92.0% were observed in the VelXLAI analysis. The amount of detected PS-2 fraction varied accordingly. Thus, it can be observed from the figures that the findings from VelXLAI program lied more close to the true concentration in both the cases. The findings from Sedfit as well as summary plot were near to each other but deviated significantly from the true concentration. Thus, the programs VelXLAI and Sedfit showed differences in analyzing more complex mixtures as compared to single component polymer samples and the detection of relative amount of components in the polymer mixture was better in VelXLAI analysis than the Sedfit analysis.

Conclusions

The aim of this study was to compare the sedimentation analysis of the bi-component polymer mixture samples prepared by different mixing ratios of the fractions by using analysis programs of VelXLAI and Sedfit. The programs showed similar results for the pure polymer sample as a function of concentration as similar peak sedimentation coefficient values and sedimentation coefficient distributions were observed. In the mixture samples, the differences were observed in the differential as well as cumulative sedimentation coefficient distributions. The Sedfit distributions were observed to shift slightly to higher sedimentation coefficient values. The amount of individual fractions of the mixture detected by two programs was significantly different. The VelXLAI analysis led to the detection of fractions near to their actual concentration, whereas in the Sedfit analysis, the low molecular weight fraction was significantly overestimated resulting in the underestimation of higher molecular weight fraction. Apart from that, the distributions for lower molecular weight fraction were broader as compared to the distributions for the higher molecular weight fraction in both the programs. The results though have been obtained from standard polymer samples; however, such a comparison is also vital in a number of commercial applications where combinations of different polymers in different weight ratios are used.

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