Flow Injection Analysis Estimation of Diffusion Coefficients of Pauci- and Polydisperse Polymers Such as Polystyrene Sulfonates

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SYNOPSIS

Flow injection analysis, often used for determination of diffusion coefficients of nonpolymeric substances, has now been applied to the characterization of pauci- and polydisperse polymers in solution. A relative method was found useful for obtaining moderate quality evaluations of diffusion coefficients and related parameters of polymers. The width at half-height $W_{1/2}$ of the trace peak is found to be proportional to the number average molecular weight $\bar{M}_n$ of pauci- and polydisperse polymers, allowing estimation of $\bar{M}_n$ and diffusion coefficients. For sodium polystyrene sulfonates at substantially infinite dilution in 1.0 g L^{-1} Na_2SO_4, a linear relation has been observed between the logarithms of the molecular weight $\bar{M}_n$ and the mean diffusion coefficient D in the $\bar{M}_n$ range of 1000–90,000 g mol^{-1} or the D range of 30×10^{-7} to 2×10^{-7} cm^2 s^{-1}.

INTRODUCTION

Flow injection analysis (FIA) has often been used for the determination of the diffusion coefficients of low molecular weight solutes in liquid solvents.[1-10]

In the present investigation it has been applied, apparently for the first time, for the estimation of diffusion coefficients and number average molecular weights of pauci- and polydisperse polymers. No publications could be found in the literature relating to the use of the FIA method to accomplish the estimation of the diffusion coefficients of *polydisperse* mixtures of polymer homologs, although Chen et al.[11,12] have recently reported on the estimation of translational diffusion coefficients of several *paucidisperse* polystyrenes in organic solvents.

The FIA method estimation for diffusion coefficients is based on the solution, by Taylor,[13,14] of the convection–diffusion equation for an increment of solute diffusing in a fluid which is in laminar flow in a cylindrical tube.

Two variants of the FIA method have been described; an absolute method, which has been well reviewed by Atwood and Goldstein,[5] and a relative method which requires calibration using a reference substance.[9,10] In the present work, experimentation has been carried out only with the latter method in view of its less demanding apparatus and procedural requirements[15] and its insensitivity to Dean flow.[10]

EXPERIMENTAL

Materials

The sodium polystyrene sulfonate samples (Pressure Chemical Co., Pittsburgh, PA) were used at a concentration of 25.0 g L^{-1} in 1.0 g L^{-1} Na_2SO_4 solvent, with a UV detector set at 254 nm. Samples with nominal number average molecular weights of the sulfonate ion of 1600, 6500, 16,000, 31,000, and 88,000 daltons (±10–15%, supplier data), hereafter designated 1.6K, 6.5K, 16K, 31K, and 88K, respectively, were studied. The polydispersity ratio, $\bar{M}_w/\bar{M}_n$, of these samples is stated by the supplier to be

Table I Characteristics of the Polystyrene Sulfonate Mixtures Studied

Sample	Parts[a]				Calculated Values	
	1.6K[b]	6.5K	31K	88K	$\bar{M}_n{}^c$	$\bar{M}_w{}^c$
A	1	4	4	1	7240	23,960
B	4	1	1	4	3660	39,590
C	4	4	1	1	3170	15,140
D	1	1	4	4	10,490	48,410
E	0	1	2	7	33,570	68,450

[a] By weight.
[b] Paucidisperse preparations sample designations. See Experimental—Reagents.
[c] Values calculated assuming that the component NaPSS preparations are monodisperse.

less than 1.10, except for the 1.6K sample, for which it was less than 1.25. We prepared polydisperse samples by mixing parts of the paucidisperse samples as indicated in Table I.

The bovine chymotrypsinogen A sample (See Table II) was used at 25.0 g L^{-1} in 0.1 M NaCl plus 0.01 M acetate buffer at pH 4.8 with the UV detector set at 280 nm.

Apparatus

The apparatus (Fig. 1) consisted of a mobile phase delivery system, a liquid chromatography (LC) sample insertion valve, a capillary diffusion tube, a constant temperature bath, a LC UV detector, and a buret to determine flow rate. The signal from the

Table II Some Characteristics of Bovine Chymotrypsinogen A (Worthington Biochemicals, Freehold, NJ, Lot CGC 37E837)

Molecular weight	25,656.4 g mol^{-1}
Diffusion coefficient D (SD)[a]	
In water, at 20°C[b]	9.50 (0.17) × 10^{-7} cm^2 s^{-1}
In solvent, at 25°C[c]	10.74 (0.21) × 10^{-7} cm^2 s^{-1}
Frictional coefficient[d]	
By sedimentation[e]	4.43 × 10^{-8} g s^{-1}
By viscosity[e]	4.27 × 10^{-8} g s^{-1}
By atomic coordinates[b]	4.38 × 10^{-8} g s^{-1}
Extinction coefficient at 280 nm[e]	2.00
Experimental $W_{1/2}{}^f$ (SD) at 30 mL h^{-1}	5.03 (0.04) min.

[a] Standard deviation.
[b] Ref. 16.
[c] Corrected from the value in water at 20°C taking into account solute concentrations and temperature.
[d] For use in Stokes–Einstein equation.
[e] Ref. 17.
[f] Width at half-height of the trace peak.

detector was sent to a strip-chart recorder and also to a computer for data storage.

Mobile Phase Delivery System

The mobile phase delivery system consisted of an argon gas cylinder with a pressure regulator which was connected by means of stainless steel tubing to an 800 mL stainless steel mobile phase reservoir. This reservoir was connected to the sample insertion valve with $\frac{1}{16}$ in. o.d. 0.8 mm i.d. Teflon tubing, equipped with a valve and with stainless steel frit filters for protection of the valve, diffusion tube and detector. The mobile phase reservoir was also connected to a 1 L steel gas pressure reservoir, which was used to minimize pressure fluctuations caused by the gas cylinder pressure regulator during the runs.

Sample Insertion Valve

The sample insertion valve was a manually actuated LC valve with a nominal 1.0 μL delivery volume (Valco Instrument Co. Houston, TX, Model CI4W.2 + 1.0).

Diffusion Tube

The diffusion tube, a 1,503 ± 1.0 cm length of nominal $\frac{1}{16}$ in. o.d. 0.8 mm i.d. Teflon tubing (Upchurch Scientific, Oak Harbor, WA) with a total volume of 7.89 ± 0.05 mL, was wound as a closely spaced single layer coil on the outside of a 2-L laboratory beaker with a 12.9 cm o.d., in such a manner that the coil diameter was close to 13.0 cm. The coil was placed in a water bath whose temperature was kept at 25.0 ± 0.1°C.

UV Absorbance

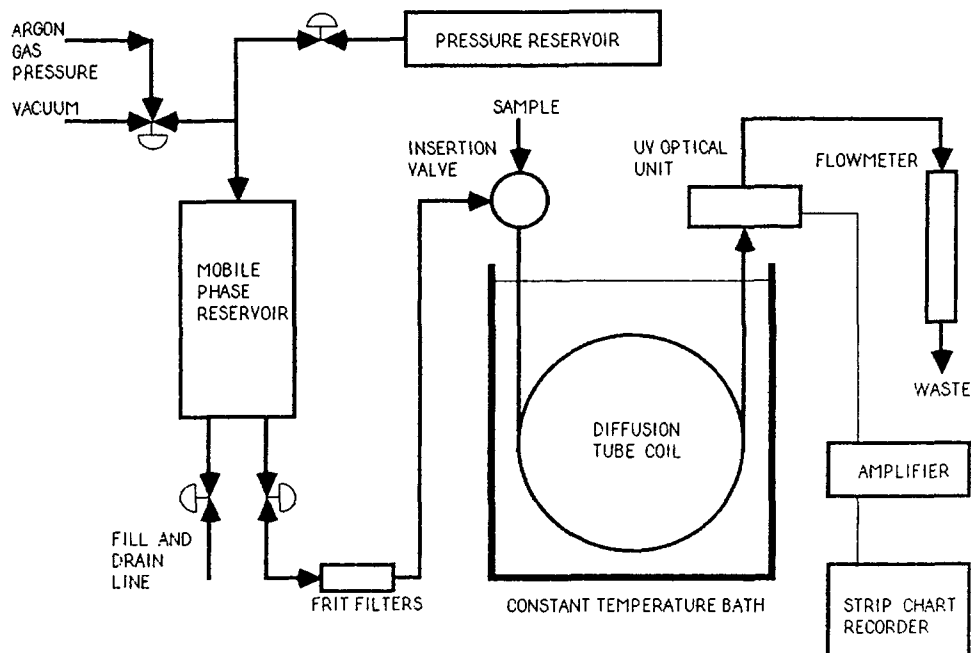The UV absorbance was measured with an ISCO Type 6 Optical Unit (ISCO, Lincoln, NE) equipped

Figure 1 Experimental apparatus for flow injection analysis.

with a flowcell with a 12-μL hold-up volume and a 2 mm light path (Cat. 68-0080-010) and with water in the reference flow cell, and a ISCO UA-5 Absorbance Monitor.

Flow Rate Measurements

The UV detector flow cell was connected, by use of $\frac{1}{16}$ in. o.d. Teflon tubing to a graduated buret which had been calibrated by dispensing water into weighing bottles. The flow rate was monitored by timing the rise of the meniscus between marks with a stopwatch.

Data Collection

The 0–1 V output from the ISCO UV detector was connected to a strip-chart recorder (Cole-Parmer Chicago, IL, Cat. 8373-30) for graphical output and, for storage of the absorbance versus time data, to an analog-to-digital channel of a DEC VAX 11/750 computer (Digital Equipment Corp., Maynard, MA). Digital data points were taken every 3 s.

Calculations

A flow rate of 30.0 mL h^{-1} was selected as standard, because of the expected D values of the sample substances of interest and the limits of eq. (3) below. At this flow rate, about four separate runs per hour can be made. Average flow rate was taken to be the

mean of the measured flow rate at the time of sample insertion and that at the peak mode. The experimental value of the width at half-height observed at this average flow rate, $W_{1/2e}$, was then corrected to that at 30.0 mL h^{-1} by

$$W_{1/2} = W_{1/2e}(F/30.0)^{0.64} \qquad (1)$$

where $W_{1/2}$ is the corrected width at half-height which was used in all subsequent calculations and graphs, $W_{1/2e}$ is the value as measured directly from the peak trace, and F is the average run flow rate, as described above. The reproducibility of the $W_{1/2}$ values was found to be within about 1% (see Table III) and the value obtained was not affected by varying the sample concentration, in agreement with the results of Vanderslice et al.[9] and Ouano.[8]

RESULTS AND DISCUSSION

The relative FIA method is based on the solution of the convection–diffusion equation by Vanderslice et al.[9] which has the following form:

$$\Delta t_B = \frac{2.58r^2 f}{D^{0.36}} \left[\frac{L}{F} \right]^{0.64} \qquad (2)$$

where Δt_B is the baseline-to-baseline time, i.e., the time interval from the moment the peak trace leaves

Table III Experimental Results for Widths at Half-Height and Diffusion Coefficients for Pauci- and Polydisperse Polystyrene Sulfonate Preparations and Comparison with Values of Liauh[18]

Samples	$W_{1/2}$ (SD)[a] at 30.0 mL h^{-1} (min)	Diffusion Coefficient in cm^2 s^{-1} × 10^7	
		Experimental (SD)	Liauh Value (±10%)
NaPSS Standards			
1.6K	3.49 (0.05)	29.65 (1.75)[b]	125.6[c]
6.5K	4.58 (0.04)	13.93 (0.61)	52.0
16K	6.39 (0.22)	5.52 (0.64)	29.5
31K	6.82 (0.07)	4.61 (0.22)	19.5
88K	9.46 (0.08)	1.86 (0.08)	10.1
NaPSS Mixtures[d]			
A	4.92 (0.03)	11.42 (0.41)	ND[e]
B	4.21 (0.07)	17.61 (1.15)	ND
C	4.07 (0.03)	19.34 (0.77)	ND
D	5.54 (0.03)	8.21 (0.28)	ND
E	7.22 (0.03)	3.94 (0.12)	ND

[a] Experimental values. Minimum of three and average of five determinations per sample.
[b] Value relative to diffusion coefficient and $W_{1/2}$ of Bovine Chymotrypsinogen A. See Table II. Uncertainties estimated by conventional error propagation methods.[19]
[c] Estimated from data presented by Liauh.[18]
[d] See Table I.
[e] Not Determined.

the baseline until the moment the trace returns to the baseline (for definition of symbols, see Nomenclature). This equation was developed from a solution using numerical methods as reported by Ananthakrishnan et al.[20] and its range of validity is given[9] as

$$0.002 \leq D\pi L/2F \leq 0.8 \qquad (3)$$

For experiments performed on the same apparatus, eq. (2) can be expressed as

$$\Delta t_B = k_1 D^{-0.36} F^{-0.64} \qquad (4)$$

Because of baseline drift, it was difficult to measure Δt_B accurately. To circumvent this problem, one of us (Buchholz) proposed using the peak $W_{1/2}$ instead of the Δt_B; as for the nearly Gaussian peaks which are usually obtained there should be a constant proportionality between these two parameters. Equation (4) thus leads to the working relationship

$$W_{1/2} = k_2 D^{-0.36} F^{-0.64} \qquad (5)$$

To test the validity of this equation with respect to our particular apparatus, runs were performed using a 6.5K polystyrene sulfonate (PSS) prepa-

ration at several different flow rates between 20 and 300 mL h^{-1}. In Figure 2, each point represents the value from a separate run. Least squares fitting of these data gives a slope of −0.62. This value is in approximate agreement with the −0.64 parameter of eq. (5), which we have used to normalize the values of $W_{1/2}$, obtained experimentally at slightly different flow rates, to the standard flow rate of 30 mL h^{-1} [eq. (1)].

Paucidisperse PSS: Estimation of Diffusion Coefficients

For experiments performed with the same apparatus and at the same flow rate but with different substances, eq. (5) becomes

$$\log D = -\frac{1}{0.36} \log(W_{1/2}) + b_1 \qquad (6)$$

Equation (6) indicates that the unknown diffusion coefficient D of a substance can be estimated experimentally be determining its $W_{1/2}$ value and using an apparatus and procedure calibrated by evaluating experimentally the $W_{1/2}$ and the equation parameters associated with a substance for which the value of D is known.
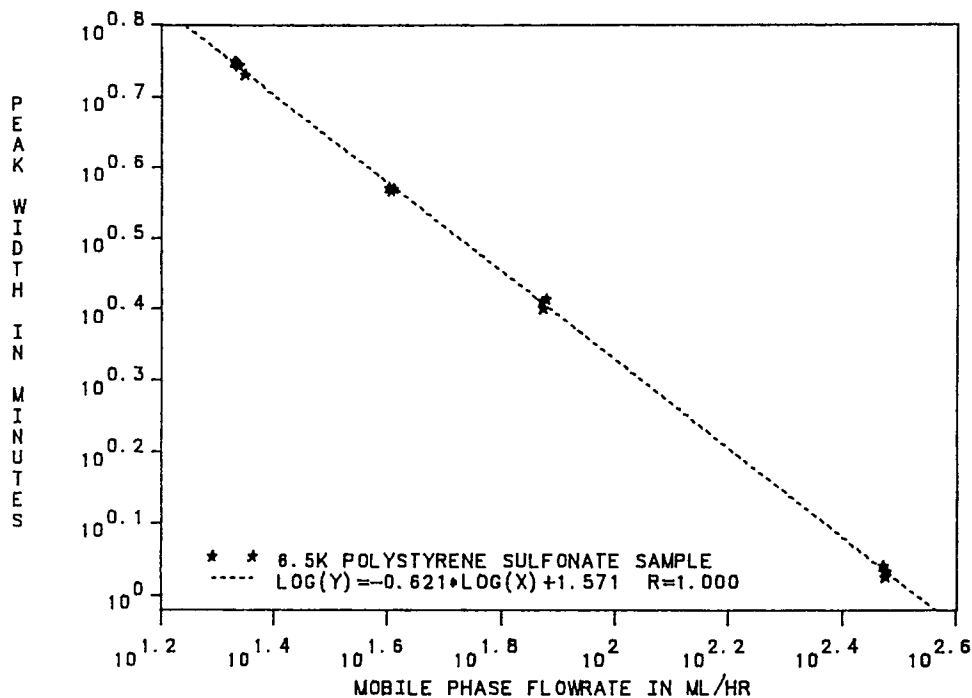
Figure 2 Reproducibility and effect of varying flow rate on the experimentally determined $W_{1/2}$ for a 6.5K NaPSS preparation in aqueous 1.0 g L^{-1} Na_2SO_4 (see Experimental—Reagents).

In our experiments, Bovine Chymotrypsinogen A (Table II), a protein of spherical molecular shape,[16,17] was employed as the reference substance, and its $W_{1/2}$ value was determined.

Experimental $W_{1/2}$ values for the paucidisperse PSS samples studied and their corresponding diffusion coefficients were determined (Table III) relative to our experimental $W_{1/2}$ value for Bovine Chymotrypsinogen A and its value of D as reported in the literature (Table II). The obtained relationship is

$$D = 10.74 \times 10^{-7}\left(\frac{5.03}{W_{1/2}}\right)^{1/0.36} \text{cm}^2\,\text{s}^{-1} \quad (7)$$

Liauh[18] has reported values of D for paucidisperse PSS samples (Table III). The values were obtained by porous capillary chromatography using the same solvent and at the same concentration as presently employed. Liauh's results are about 1 order of magnitude larger than ours. Based on the now reported work and on some preliminary quasistatic light scattering data for NaPSS samples obtained by one of us (Boyle), we believe that Liauh's results are substantially in error.

Paucidisperse PSS: Molecular Weight Relationships

The relationship between the molecular weight M and D in the diffusion of a spherical molecular species in a liquid medium according to the Stokes–Einstein equation[2] is

$$M = \frac{4}{3}\pi R_0^3\rho = \frac{4}{3}\pi\rho\left[\frac{kT}{6\pi\mu D}\right]^3 \quad (8)$$

and, for a series of polymers of the same family but of different molecular weight,

$$M = k_3 D^{-E} \quad (9)$$

where E is a parameter specified by the shape of the molecules diffusing (see below). This relation is valid for low molecular weight species.[21,22]

Combining eq. (6) and (9) yields

$$\log M = \frac{E}{0.36}\log(W_{1/2}) + k_4 \quad (10)$$

where, for a particular apparatus, flow rate and family of polymer homologs, E and k_4, should be con-

stants. Therefore, eq. (10) indicates that the FIA method can be used for estimation of molecular weights.

The presently obtained $W_{1/2}$ values for a series of *paucidisperse* PSS preparations of known molecular weight (Table III) were plotted on logarithmic–logarithmic scales against their known molecular weights and the relationship was found to be approximately linear (Fig. 3). The departures of individual points from linearity probably arise mainly because of the uncertainties in their reported molecular weights.

Polydisperse PSS: Number Average Molecular Weights

Polydisperse PSS samples were prepared by mixing known masses of several paucidisperse samples of known $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values (Table I). We calculated[23] the number average $\bar{M}_n$ and weight average $\bar{M}_w$ molecular weights of the mixtures (Table III).

Values of $W_{1/2}$ were determined experimentally for these mixtures. No significant correlation is found between the $W_{1/2}$ and the weight average molecular weight $\bar{M}_w$ of the mixtures (Fig. 3). With

$\bar{M}_n$, however, a good correlation is obtained and the corresponding line is nearly the same as that found for the paucidisperse standards. Thus the *number* average molecular weight $\bar{M}_n$, appears to be appropriate for use in eqs. (9) and (10). For the experimental conditions used presently and for *both* the pauci- and polydisperse samples now studied, eq. (10) can be expressed as

$$\log \bar{M}_n = (3.99) \log(W_{1/2}) + 1.08, \quad R = 0.992(11)$$

The correlation coefficient for the mixtures line is found to be slightly better than that for the standards probably because the uncertainties in the molecular weights of the standards compensate out in the mixtures.

Thus, the number average molecular weight $\bar{M}_n$, of polydisperse polymer fractions can be estimated by use of the FIA procedure, provided that suitable homolog fractions are available, and their $\bar{M}_n$ is known. Even if fractions of known $\bar{M}_n$ are not available, the procedure may be of use in assigning *relative* $\bar{M}_n$ values to a series of experimental samples of polymeric fractions, or as a method to reduce the uncertainty in $\bar{M}_n$ values obtained by other methods.
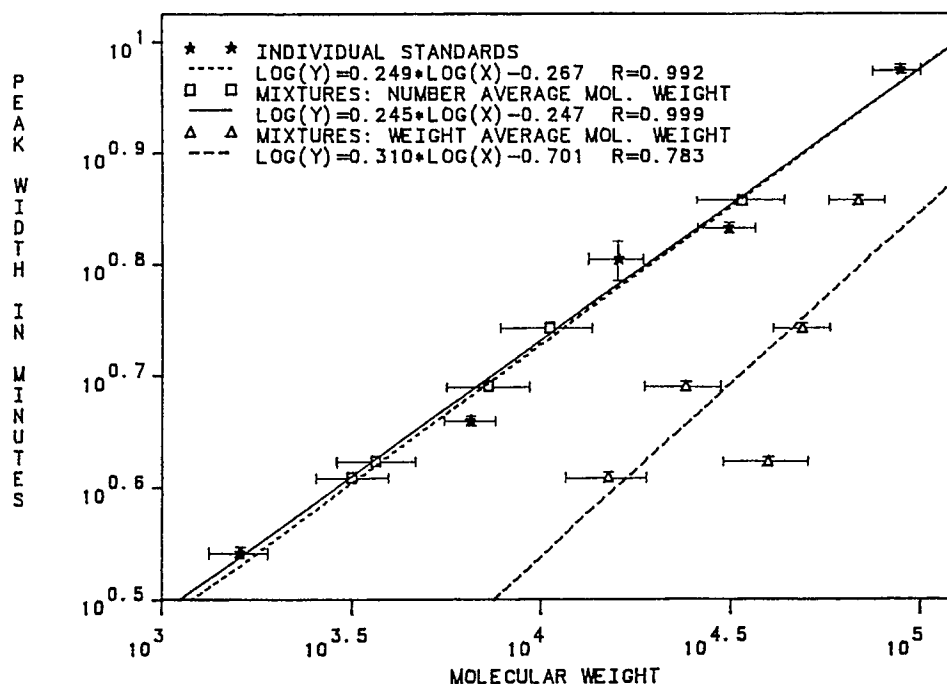

Figure 3 NaPSS samples. Correlation of the experimental $W_{1/2}$ (values corrected to a flow rate of 30.0 mL h^{-1}) with the nominal molecular weights of NaPSS standards, and with the number and weight average molecular weights of prepared NaPSS mixtures. The horizontal and vertical error bars represent one standard deviation (Tables I and III).

Polydisperse PSS: Number Average Diffusion Coefficients

The relationships developed above suggest that the apparent diffusion coefficient of a polymeric mixture, $\bar{D}$, can be calculated from known values of the diffusion coefficient D_i, the molecular weight M_i, and the weight fraction w_i of each of the components of the mixture.

Since the relationship between the logarithms of $\bar{D}$ and $W_{1/2}$ (and therefore of $\bar{M}_n$) is linear over the range of conditions studied, then

$$\log \bar{D} = -\frac{1}{E} \log \bar{M}_n + b_2 \qquad (12)$$

If the molecular weights M_i and the diffusion coefficients D_i are known for at least two adequately separated paucidisperse fractions in a homolog series, then the slope $k_5 = (\Delta \log D_i / \Delta \log M_i)$, and the intercept b_2, can be estimated.

Equation (12) for $\bar{D}$ apparently should also be valid for any mixture of polydisperse fractions, using the $\bar{D}$ values for the individual component fractions instead of the D_i, and their $\bar{M}_n$ values instead of the M_i in the usual equations for $\bar{M}_n$.

Polydisperse Polymers: Molecular Weight and $W_{1/2}$ Relationships

Using the available measurements of $W_{1/2}$ for the individual paucidisperse polymers and for the known-composition mixtures of these, trial calculations were carried out to discover the appropriate mixing rule for $W_{1/2}$. It was found that the experimental and calculated $W_{1/2}$ values for the mixtures could be brought into approximate agreement by considering the number average of the molecular weights of the components present.

A theoretical explanation for this interesting result was kindly derived for us by Eichinger[24] using the argument presented in the Appendix. The derived relation between the molecular weight and $W_{1/2}$ for a polydisperse polymer mixture is given by

$$\bar{M}_n \propto (\bar{W}_{1/2})^\eta \qquad (13)$$

and this relationship appears to be in agreement with the results of the present experimentation, where it is found, for the polymer mixtures studied, that $\eta = 3.82$.

Polydisperse Polymers: Diffusion Coefficient and $W_{1/2}$ Relationships

Based upon the development described and the condition stated in the Appendix, i.e., $\gamma \Rightarrow 1$, then the $\bar{W}_{1/2}$ property of polydisperse polymers can be predicted approximately from the $W_{1/2i}$ (or $\bar{W}_{1/2i}$) values and the masses w_i of the paucidisperse (or polydisperse) components of the mixture by use of an equation of the form

$$(\bar{W}_{1/2})^{-\eta} = \sum_{i=1}^{N} w_i (W_{1/2i})^{-\eta} \bigg/ \sum_{i=1}^{N} w_i \qquad (14)$$

Thus, a general relationship for the apparent diffusion coefficient $\bar{D}$ of polydisperse mixtures in terms of the diffusion coefficients D_i, of the paucidisperse (or polydisperse) component fractions is

$$\bar{D}^E = \sum_{i=1}^{N} w_i D_i^E \bigg/ \sum_{i=1}^{N} w_i \qquad (15)$$

where $E = (0.36)(\eta)$.

Significance of the Exponent E

The value of the exponent E should depend on the shape of the diffusing molecules; e.g., 3 for spherical molecular species, 2 for ideal flexible polymer chains, 1 for perfectly rigid polymer chains, and other values for ellipsoidal molecules.[25]

For the polydisperse PSS mixtures studied, A, B, C, D, and E (Tables I and III), the experimental values obtained for the exponent E [eq. (14)] are 1.31, 1.57, 1.41, 1.34, and 1.25, respectively, and the average value is 1.38 ± 0.12. For the paucidisperse PSS standards [eq. (10)] the value is 1.42 ± 0.08.

The observed value of E might be taken to indicate that the observed polymers have moderately stiff chains, or have ellipsoidal molecules whose degree of eccentricity is proportional to their molecular weight,[25] or may also indicate an effect of the laminar shear field.[26]

Applicability of the FIA Method

The now-reported FIA procedure appears to be generally applicable to assist in the characterization of polymer homolog families. In work being reported separately, we have applied the procedure to provide estimates of the diffusion coefficients and molecular

weights of a number of polydisperse lignin sulfonate and kraft lignin preparations.[15]

NOMENCLATURE

b_1, b_2	constants
D	diffusion coefficient ($cm^2 s^{-1}$)
$\bar{D}$	apparent diffusion coefficient of a mixture
D_i	diffusion coefficient of component i
E	molecular shape parameter
F	volumetric flow rate ($cm^3 s^{-1}$)
f	apparatus constant
k	Boltzmann's constant
k_1, k_2, k_3, k_4	constants
L	length of diffusion tubing (cm)
M	molecular weight
M_i	molecular weight of component i
$\bar{M}_n$	number average molecular weight
$\bar{M}_w$	weight or mass average molecular weight
R_0	molecular radius
r	inside radius of tubing (cm)
T	absolute temperature
$W_{1/2}$	width at half-height of trace peak (s)
$W_{1/2e}$	experimental $W_{1/2}$ at F different from 30 mL h^{-1}
$\bar{W}_{1/2}$	$W_{1/2}$ for a polydisperse mixture
w_i	parts by weight of component i in a mixture
X_i	mole fraction of component i
$\alpha, \beta, \gamma, \eta$	exponents
Δt_B	the baseline-to-baseline time (s)
μ	viscosity of solvent or mobile phase
ρ	density of particles

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APPENDIX

Derivation of the Relation between Molecular Weight and $W_{1/2}$ for Polydisperse Polymers[24]

From the Stokes–Einstein equation, the relationship between the diffusion coefficient D and the hydraulic radius R_0, can be written as

$$D \propto 1/R_0 \qquad (A.1)$$

R_0 is related to the molecular weight as

$$R_0 \propto M^\alpha \qquad (A.2)$$

where $\alpha = 0.5$ for a theta solvent and may be 0.6 for a good solvent, and, for polymers which depart increasingly from a random coil, the parameter α approaches unity. Combining eqs. (A.1) and (A.2) gives

$$D \propto M^{-\alpha} \qquad (A.3)$$

For the relative FIA procedure used, eq. (6), as reported by Vanderslice,[9] may be expressed as

$$D \propto (W_{1/2})^{-1/\beta} \qquad (A.4)$$

where $W_{1/2}$ is the width at half-height of the bolus's trace and the numerical value of the exponent is reported to be $\beta = 0.36$. Combining eqs. (A.3) and (A.4) and rearranging give

$$W_{1/2} \propto M^{\alpha\beta} \qquad (A.5)$$

Since it was found that, in the present experimentation, a log–log relationship prevails between $W_{1/2}$ and M, we find it useful to raise the terms on both sides of eq. (A.5) to a power $-\eta$:

$$(W_{1/2})^{-\eta} \propto M^{-\alpha\beta\eta} \qquad (A.6)$$

where the exponents, taken together, may be represented as $\gamma = \alpha\beta\eta$.

For a theta solvent, $\gamma = (0.5)(0.36)(3.82) = 0.69$. With solvents for which $\alpha = 0.6$–0.73, $\gamma = 0.83$–1.0.

If molecules of differing molecular weight are present, the weight average of both sides of eq. (A.6) can be represented as

$$(\bar{W}_{1/2})^{-\eta} \propto \sum_{i=1}^{N} (M_i)^{-\gamma} M_i X_i \bigg/ \sum_{i=1}^{N} M_i X_i \qquad (A.7)$$

or:

$$(\bar{W}_{1/2})^{-\eta} \propto \sum_{i=1}^{N} M_i^{(1-\gamma)} X_i \bigg/ \sum_{i=1}^{N} M_i X_i \qquad (A.8)$$

As the numerical value of γ approaches unity, the power to which M_i is raised in the numerator approaches zero and the value of the numerator approaches unity also.

As this limiting value, eq. (A.8) reduces to:

$$(\bar{W}_{1/2})^{-\eta} \propto 1/\bar{M}_n \qquad (A.9)$$

or

$$\bar{M}_n \propto (\bar{W}_{1/2})^{\eta} \qquad (A.10)$$